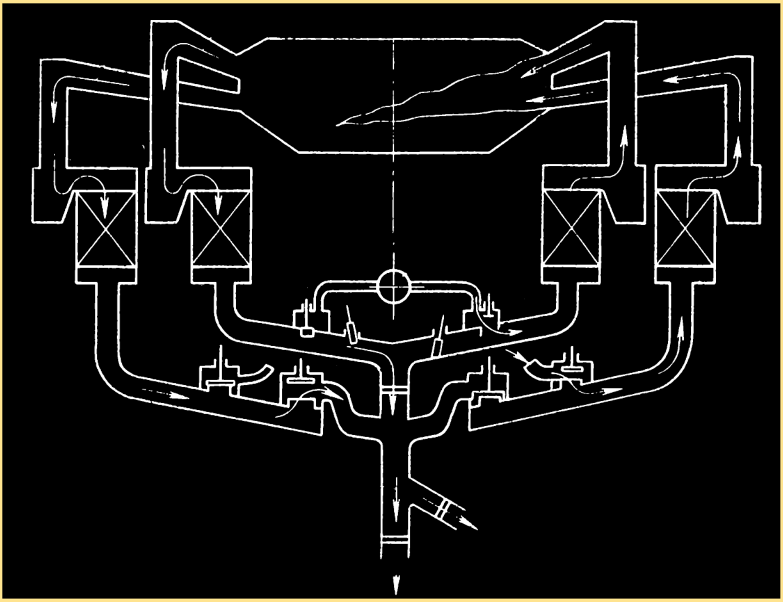
G. OIKS

CONVERTER AND OPEN-HEARTH STEEL MANUFACTURE



Г. Н. Ойкс

ПРОИЗВОДСТВО СТАЛИ
(ОСНОВЫ ТЕОРИИ И ТЕХНОЛОГИЯ)

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CONVERTER AND OPEN-HEARTH STEEL MANUFACTURE

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The Greek Alphabet

Αα	Alpha	Ιι	Iota	Ρρ	Rho
Ββ	Beta	Κϰ	Kappa	Σσ	Sigma
Γγ	Gamma	Λλ	Lambda	Ττ	Tau
Δδ	Delta	Μμ	Mu	Υυ	Upsilon
Εε	Epsilon	Νν	Nu	Φφ	Phi
Ζζ	Zeta	Ξξ	Xi	Χχ	Chi
Ηη	Eta	Οο	Omicron	Ψψ	Psi
Θθϑ	Theta	Ππ	Pi	Ωω	Omega

На английском языке

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Preface

New production plans adopted in the USSR envisage still greater increase in the production of steel and improvement of its quality. To fulfil the task, it is planned to further expand the construction of oxygen-converter shops since only this approach can enable a rapid growth of production capacities.

Alongside the introduction of top-blown oxygen converters of sizes 130, 250, and 400 tons, the use of other versions of oxygen-converter process is contemplated, aimed at attaining higher productivity and increasing the percentage of solid scrap in the charge. It is known from experience that the proportion of scrap in converter charges can be increased up to 35 per cent and more by adding silicon or calcium carbides to the charge or by preliminarily heating steel scrap.

The trend to intensify metal blowing in Bessemer converters requires that the composition of pig iron, the sizes and density of steel scrap, and the quality of lime (as regards its CaO content and porosity) be standardized more rigorously.

Though the proportion of steel produced in oxygen-blown Bessemer converters is continuously increasing in the USSR, the share of open-hearth steel in the total steel production will remain appreciably large for the next two decades. For that reason, the work aimed at intensification of the open-hearth process will be continued. Conversion of open-hearth furnaces to natural gas firing makes it possible to improve furnace construction, increase the area of hearth, and replace the complicated ports having a high resistance to gases by simpler single-channel ports which have a lower resistance to combustion products and are easily accessible for repairs.

The productivity of open-hearth furnaces can be increased almost twice by intensifying the melting process, in particular, by blowing the bath with oxygen. The possibilities of controlling the compositions of slag and metal by their carbon content can be substantially widened by blowing-in powdered materials and carburizers. The processing with synthetic slags and blowing of argon into metal extend the possibilities of degassing and desulphurization of steel and its purification from non-metallic impurities. Modern methods of steel deoxidation by exothermic ferro-alloys and fluxed ferro-alloy briquettes make it possible to save ferro-alloys, refine the metal more deeply, and thus improve the quality of steels.

Wide use of technical oxygen in the open-hearth manufacture of steel has opened ways for developing new processes of steel production in twin-bath furnaces and continuous plants.

These are only some of the new trends of engineering progress in steelmaking.

In the complex process of production control, the steelmaker, foreman, and process engineer play principal roles: their skill and activity determine the correct organization of production.

This book is intended for steelmakers and shop foremen. It discusses the newest achievements of science and technology in the field of steel production, lays out some laws of physical chemistry by which the chemical reactions in the metal proceed, and shows the ways for controlling these reactions.

Chapter One

IRON, RELATED METALS, AND IMPURITIES

THE NATURE AND PROPERTIES OF IRON

The melting point of chemically pure iron is 1539°C; the radii of γ-Fe and α-Fe atoms are respectively equal to 1.26 Å and 1.23 Å*.

As has been shown by Russian scientist A. G. Stoletov in 1889, the specific properties of metals are due to the behaviour of their outer-shell (valence) electrons which are only weakly bonded with the nucleus; they can easily detach from and leave the atom, and also jump to outer shells of other atoms. These valence electrons are termed free electrons**. In a metal composed of a tremendous number of atoms, free electrons are found to be almost at the same distance both from the nucleus of the atom in whose orbit they should move and a neighbouring atom, so that they can go into the neighbouring orbit. By giving up their electrons, atoms become positively charged ions. Valence electrons do not belong to a particular atom, but are collectivized into an electron cloud moving with a tremendous velocity in the volume of metal. The paths of electrons around each nucleus cannot be observed.

An essential feature inherent in metal only is what is called the metallic bond noted for a weak bondage between the outer-shell electrons and the nucleus. The interaction of outer-shell electrons of various atoms forms bondage forces (cohesion forces) between atoms of a metal, as a result of which the ions in crystal lattices hold their positions due to the electron cloud. Collectivization of valence electrons is the basis of the metallic bond. This structure of metal is shown in Fig. 1.

---

* Å (angström) = 10^{-8} cm.

** In non-metals, outer-shell electrons are strongly retained by the atoms.

Iron exhibits both thermal and electric conduction, i.e., clearly expressed metallic properties. On melting of pure iron, variations of its enthalpy (ΔH 3560-3700 cal/g-atom), enthropy ($\Delta S = 1.97$-2.04 cal/degree) and thermal capacity are insignificant, which makes it possible to suppose that qualitative changes occurring on melting are negligible and that the thermal motion of atoms in solids is very similar to that in liquids. The density γ of molten iron is 6.9-7.0 g/cm^3. The surface tension σ of liquid iron in contact with an inert gas is 1870-1836 erg/cm^2.

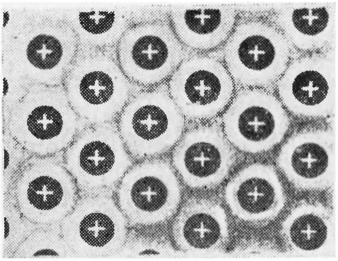

Fig. 1. Schematic structure of a metal (positive ions are at the nodes of the lattice and free electrons move in voids between them)

Perfectly pure iron cannot be produced industrially. Iron of a purity of 99.9917 per cent was obtained under laboratory conditions. In analysing iron for impurities (0.0083 per cent), it was found that iron contains a large number (27) of elements, including carbon, silicon, manganese, sulphur, phosphorus (constant companions of iron) and other latent impurities (H, N, O, Ca, Mg, etc.). Any impurity changes the properties of iron. For instance, an increase of the carbon content from 0.02 to 0.10 per cent reduces the thermal conductivity of iron from 0.177 cal/cm·s·°C down to 0.134 cal/cm·s·°C. Nonmetals (phosphorus, sulphur, oxygen, hydrogen, and nitrogen), even when present in insignificant quantities in iron, affect the properties of iron much more appreciably than its related metals, i.e., copper, nickel, manganese, etc. Pure iron practically has no industrial applications. It possesses a high malleability, but a poor hardness, which cannot be improved by hardening, since iron is unhardenable. For that reason the study of the forms of existence of impurities, i.e., the nature of the solutions of carbon, oxygen, and other elements in molten iron, is of great importance.

FORMS OF EXISTENCE OF IMPURITIES IN IRON

When a metal solidifies, its atoms are disposed in the space in a geometrically ordered pattern in the form of elementary crystal lattices.

Figure 2 shows the types of crystal lattices in solid metals. The body-centred (cubic) lattice (Fig. 2*a*) contains nine atoms (eight at the vertices of the cube and one in the centre). But, if, for instance, a crystal is composed of a million of such elementary cells, it does not mean that it contains nine million atoms. A corner (node) atom in each elementary cell simultaneously belongs to eight cells; therefore, one cell possesses only 1/8 of each node atom, and only the central atom fully belongs to a given cell.

Thus, an elementary lattice of this type possesses 8 × × 1/8 + 1 = 2 atoms. A metallic crystal composed of a million of such cells contains around two millions of atoms (the edge atoms at the surface of the crystal are not surrounded from all sides by neighbouring atoms). This number is tremendous, since, if we imagine a real crystal of iron of this crystalline structure with the side of cube of 1μm (0.001 mm), it will contain more than 10 such cells. The body-centred (cubic) lattice is found in such solid metals as Li, Na, K, V, Cr, α-Fe, Rb, Nb, Mo, W, etc.

The face-centred (cubic) lattice (Fig. 2*b*) contains 14 atoms (eight at the vertices and 6 at the faces of the cube). A cell of this crystal lattice possesses four atoms on the average, since each corner atom simultaneously belongs to eight elementary cells; each atom in the centre of a face belongs to two neighbouring atoms, and there is no atom in the centre of the cell. Therefore, one elementary cell of the crystal lattice of this type possesses 8 × 1/8 + 6 × 1/2 = 4 atoms. This type of lattice is characteristic of such metals as Al, Ca, γ-Fe, Ni, Cu, Pd, Ag, Pt, Au, Pb, etc.

The hexagonal close-packed lattice (Fig. 2*c*) contains 17 atoms. A cell of this crystal lattice possesses six atoms, since two atoms at the centres of the hexagons simultaneously belong to two neighbouring cells (2 × 1/2 = 1 atom); 12 atoms at the vertices of the prism simultaneously belong to six neighbouring cells (12 × 1/6 = 2 atoms); and three atoms inside the prism fully belong to the given cell only.

Mendeleev's Periodic

Elements in groups 0; Ia, b,
and VIII are written in increasing

Symbols
- □ Face-centred cubic (f.c.c.)
- ⊡ Body-centred cubic (b.c.c.)
- ⊠ Diamond lattice
- ⊞ Complex multi-atom cubic
- ⬡ Hexagonal
- ⏣ Close-packed hexagonal (c.p.h.)
- ▯ Tetragonal
- ◇ Orthorhombic

Periods									
1	(H 1) ⬡ Hydrogen								
2	Li 3 ⊡ Lithium								
3	Na 11 ⊡ Sodium		Transient groups						
4	K 19 ⊡ Potassium	Ca 20 □ ⏣ Calcium	Sc 21 ⬡ Scandium	Ti 22 ⏣ ⊡ Titanium	V 23 ⊡ Vanadium	Cr 24 ⊡ Chromium	Mn 25 ⊞ ⊞ ⬡ Manganese	Fe 26 ⊡ □ Iron	Co 27 ⏣ □ Cobalt
5	Rb 37 ⊡ Rubidium	Sr 38 □ Strontium	Y 39 ⏣ Yttrium	Zr 40 ⏣ ⊡ Zirconium	Nb 41 ⊡ Niobium	Mo 42 ⊡ Molybdenum	Tc 43 ? Technetium	Ru 44 ⏣ Ruthenium	Rh 45 □ Rhodium
6	Cs 55 ⊡ Caesium	Ba 56 ⊡ Barium	La* 57 Lanthanum	Hf 72 ⬡ Hafnium	Ta 73 ⊡ Tantalum	W 74 ⊡ Tungsten	Re 75 ⏣ Rhenium	Os 76 ⏣ Osmium	Ir 77 □ Iridium
7	Fr 87 ? Francium	Ra 88 ? Radium	Ac 89 ? Actinium	Actinoids					
				Th 90 □ Thorium	Pa 91 ? Protactinium	U 92 ◇ Uranium	Np 93 Neptunium	Pu 94 Plutonium	Am 95 Americium

*Rare earths

Ce 58 Cerium	Pr 59 Praseodymium	Nd 60 Neodymium	Pm 61 Promethium	Sm 62 Samarium	Eu 63 Europium	Gd 64 Gadolinium

Fig. 3. Mendeleev's Per

able of the Elements

IIa, b; IIIa, b; IVa, b; Va, b; VIa, b; VIIa, b,
rder of electrons in atoms

							H 1 ⬡ *Hydrogen*	**He** 2 ? *Helium*
		Be 4 ⏣ *Beryllium*	**B** 5 ? *Boron*	**C** 6 ⊠⬡ *Carbon*	**N** 7 ⬡⊞ *Nitrogen*	**O** 8 ⊞◇ *Oxygen*	**F** 9 ? *Fluorine*	**Ne** 10 □ *Neon*
		Mg 12 ⏣ *Magnesium*	**Al** 13 □ *Aluminium*	**Si** 14 ⊠ *Silicon*	**P** 15 ◇ *Phosphorus*	**S** 16 ◇ *Sulphur*	**Cl** 17 ▯ *Chlorine*	**Ar** 18 □ *Argon*
Ni 28 □ *Nickel*	**Cu** 29 □ *Copper*	**Zn** 30 ⏣ *Zinc*	**Ga** 31 ◇ *Gallium*	**Ge** 32 ⊠ *Germanium*	**As** 33 ◇ *Arsenic*	**Se** 34 ⬡ *Selenium*	**Br** 35 ◇ *Bromine*	**Kr** 36 □ *Krypton*
Pd 46 □ *Palladium*	**Ag** 47 □ *Argentum*	**Cd** 48 ⏣ *Cadmium*	**In** 49 ▯ *Indium*	**Sn** 50 ⊠▯ *Tin*	**Sb** 51 ◇ *Antimony*	**Te** 52 ⬡ *Tellurium*	**I** 53 ◇ *Iodine*	**Xe** 54 □ *Xenon*
Pt 78 □ *Platinum*	**Au** 79 □ *Gold*	**Hg** 80 ◇ *Mercury*	**Tl** 81 ⏣□ *Thallium*	**Pb** 82 □ *Lead*	**Bi** 83 ◇ *Bismuth*	**Po** 84 ⬡ *Polonium*	**At** 85 ? *Astatine*	**Rn** 86 ? *Radon*

Cm 96 *Curium*	**Bk** 97 *Berkelium*	**Cf** 98 *Californium*	**En** 99 *Einsteinium*	**Fm** 100 *Fermium*	**Md** 101 *Mendelevium*	**No** 102 *Nobelium*	**Lr** 103 *Lowrencium*	**Ku** 104 *Kurchatovium*

(lanthanides)

Tb 65 *Terbuim*	**Dy** 66 *Dysprosium*	**Ho** 67 *Holmium*	**Er** 68 *Erbium*	**Ty** 69 *Thulium*	**Yb** 70 *Ytterbium*	**Lu** 71 *Lutecium*

odic Table of Elements

An elementary cell is further characterized by the coordination number, which is understood as the number of nearest equidistant atoms around a chosen atom. For instance, in the body-centred lattice (see Fig. 2), the central atom is at the closest equal distances from the eight atoms located at the vertices (nodes) of the cube, i.e. the coordination number of this lattice is equal to eight (C8).

For other types of lattices, the coordination numbers are: C12 for the face-centred cubic lattice; H12 for the hexagonal close-packed lattice; and H6 for the less densely packed hexagonal lattice.

Carbon in Iron. As is known, the concentration of carbon dissolved in iron in the form of atoms C or ions C^{+4} determines the name of the alloy produced (pig iron, steel, or soft iron). Iron belongs to polymorphous metals, i.e. its elementary crystal lattice may be different at different temperatures (various allotropic modifications are formed).

Iron has three allotropic modifications. At temperatures below 910°C it is α-Fe, having the body-centred cubic lattice and coordination number C8. At a temperature of 910°C atoms of iron rearrange into the face-centred cubic lattice of γ-Fe, which has the coordination number C12 (corresponding to the densest packing of "spheres" of equal size in space); this modification exists within the temperature range of 910-1401°C. At 1401°C, atoms of iron again rearrange from the face-centred lattice into the body-centred cubic lattice of δ-Fe having the coordination number C8. This modification is stable at temperatures between 1401° and 1539°C and probably remains such after a certain superheating.

The temperature at which one allotropic modification is changed for another is termed the point of allotropic (polymorphous) transformation. At 768°C, (the Curie point), iron loses its magnetic properties without changing the crystal lattice. The non-magnetic modification of iron existing within the temperature range of from 768° to 910°C is termed β-Fe. Gamma-iron (γ-Fe) is also non-magnetic.

Data on atomic structures of iron melts are not available. But it may be assumed that at temperatures near the melting point and solidification point the crystal lattice structure of short-range order for pure iron and low-carbon steel is similar to that of δ-Fe (C8), while with an increase of carbon content the structure becomes similar to that of the lattice of γ-Fe (C12). The structure of a liquid metal near its solidification point may be considered under an assumption that the same electrostatic forces which determine interatomic distances in crystals are acting also in the liquid. Therefore, we can suppose that the least interatomic distance in a liquid metal is close to the interatomic distance in crystals of that metal. But the number of atoms present in the volume considered will not be the same, since the volume of metal in a liquid state at the melting point is greater by 2-6 per cent than that in the solid state, so that the interatomic distances increase upon melting almost for all metals. Thus, the metals which in a solid state are characterized by crystal lattices with coordination numbers C12 and C8, in a molten state will have the numbers of the "nearest neighbours", respectively 11 and 7, which indicates that the structure of a liquid is less dense and less ordered than the structure of a crystal, i.e., the liquid is more "loose".

In a solid crystal, ions are always in an oscillating motion about their mean positions; they may change places and pass into the space between nodes. At these moments, the nodes of the lattice remain vacant. Oscillations of atoms depend on temperature, the amplitude of oscillations of an atom being the greater, the higher the temperature is. Some atoms may possess an energy far exceeding the mean energy of an atom. Such atoms have a large amplitude of oscillations and can easily move from one place to another, for instance, from a node to internode space or from a face of a crystal to another cell. At a substantial increase of temperature and at the melting point, the interatomic (ionic) bonds are weakened and, owing to motion of atoms leaving nodes, an ever greater number of voids (holes) are formed in the structure of a liquid metal.

Atoms of the impurities dissolved in iron are located at the nodes of an elementary cell or intrude inside the lattice and locate between the atoms of the basic metal (solvent). The former case refers to the formation of a substitutional solid solution, and the latter to an interstitial solid solution. If the atoms of the component being dissolved replace the atoms of iron and occupy their positions at the nodes of the lattice, then the interatomic distances in an elementary cell may either increase or decrease depending on the ratio of atomic radii (Fig. 4). If an interstitial solution is formed, the interatomic distances always increase.

The solubility of carbon in α-Fe is extremely poor, being 0.025 per cent at 723°C and as low as 0.006 per cent at room temperature. The maximum content of carbon in austenite at equilibrium with cementite is 2.06 per cent, and at equilibrium with graphite, 2.03 per cent.

The solubilities of elements in liquid melts depend on many factors. It has been found that if the atomic radii and melting points of two metals differ sharply, these elements are only limitedly soluble in each other. On the contrary, if two metals have almost the same atomic radii and melting points and if the components are isomorphous, i.e., similar in their properties, composition and shape, then they are usually unlimitedly soluble in each other, though there are some exceptions from this rule.

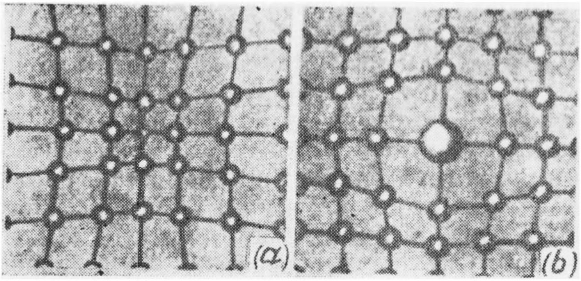

Fig. 4. Distortions of crystal lattice in a substitutional solid solution:

a—atoms of solvent are larger than atoms of the element dissolved; *b*—atoms of solvent are smaller than atoms of the element dissolved

Metals having the same type of crystal lattice are soluble in any proportions in each other, provided that the atomic radii and lattice parameters of the impurity and solvent differ by not more than 10-15 per cent. Substitutional solid solutions in iron-based alloys may form unlimitedly if the atomic radii of the elements being dissolved differ from that of the solvent by not more than 8 per cent. With a greater difference (from 8 to 15 per cent), only limited solid substitutional solutions can be formed. Non-metals, which have small atomic radii, form interstitial solid solutions.

The solubility of carbon in α-Fe is substantially lower than that in γ-Fe, despite the fact that the interatomic space in the elementary cell of α-Fe is much greater (32 per cent) than that in γ-Fe (26 per cent). Since the atoms and lattice parameters of carbon and iron differ substantially from each other, carbon atoms cannot form a substitutional solid solution in iron.

Interstitial phases are formed through interaction of transient metals (Fe, Co, Mn, Mo, V, Ti, Zr) with non-metals (B, C, H, N, O) which are characterized by small atomic radii. Thus, if the ratio of the atomic radius of a non-metal to that of a transient metal is less than 0.59, then interstitial solutions (borides, carbides, hydrides, nitrides) are formed, i.e., these elements form interstitial solid solutions in iron. Non-metallic atoms are located in "voids" between metallic atoms and connected by metallic (ionic) or covalent bonds with the latter. With the formation of an interstitial solid solution, the crystal lattice is distorted more appreciably than in the case of a substitutional solid solution.

Thus, on dissolution of carbon in iron interstitial solid solutions α-Fe and γ-Fe are formed. In the γ-Fe lattice, a carbon atom is in the centre of an elementary cell; in the α-Fe lattice a carbon atom is in the centre of a face. With the packing characterized by the coordination number C12, the radius of iron atom is 1.26 Å, while with C8, it is equal to 1.23 Å. The distance between the centre of a void and the centres of the nearest atoms of iron is 1.59 Å for α-Fe and 1.78 Å for γ-Fe.

The size of the remaining void for α-Fe is $1.59\ \text{Å} - 1.23\ \text{Å} = 0.36\ \text{Å}$, and that for γ-Fe $1.78\ \text{Å} - 1.26\ \text{Å} = 0.52\ \text{Å}$.

The possibility for atoms to penetrate into the lattice can be calculated in a different way: the γ-Fe lattice can accommodate a sphere of a radius of $0.41\ r$ and the α-Fe lattice, a sphere of a radius of $0.29\ r$ (r being the radius of the atom of iron in angströms); thus, it will be seen that crybeing linked into a typical metallic bond with the atoms of the solvent and electron gas, i.e., they give up their valence electrons into the total mass of the electron cloud and are present in the form of ions.

Sulphur in Iron. The radius of a sulphur atom is 1.05 Å. Sulphur is a typical metalloid. It easily acquires two electrons to form an ion S^{2-}. The coefficient of diffusion of sulphur in liquid iron is 0.74×10^{-4}, 13×10^{-4}, $1.9 \times \times 10^{-5}$ cm²/s, according to various experimental data. Sulphur has a strong surface activity both in binary (Fe-S) and ternary (Fe-C-S; Fe-Si-S) alloys. It has been concluded from the results of numerous studies that sulphur can exist in two forms in molten iron: in one case it forms an interstitial solution in iron; in the other, it forms not only interstitial solutions, but also partially substitutional solutions. It has been found that the activity of sulphur increases substantially when carbon and silicon are present in the melt. This explains why pig iron can be desulphurized more readily than steel.

According to a wide-spread view, sulphur forms groups (quasi-molecules) of Fe-S in liquid iron. It is unlimitedly soluble in liquid iron. It is assumed that sulphur forms an interstitial solution with iron.

Phosphorus in Iron. It is assumed that Fe-P groups similar to Fe_2P molecules may be present in liquid iron containing phosphorus. Phosphorus has a high surface activity and saturates the surface layers of metal even at its low concentrations in the solution. But in Fe-C-P alloys phosphorus loses its surface activity in the presence of manganese, which is explained by the formation of stable groups, similar to Mn_5P_2 molecules, in the melt. It is still unclear how these groups (or Fe_2P molecules in a solution with iron) are located and oriented in an elementary lattice. According to Acad. N. T. Gudtsov, phosphorus atoms form interstitial solutions with iron.

Oxygen in Iron. It was earlier believed that oxygen can be present in liquid iron in the form of molecules of ferrous oxide FeO. In later studies it has been shown that oxygen can probably exist in the form of O^{2-} ions in the iron melt. The radius of an oxygen ion is 1.32 Å (i.e., substantially greater than that of carbon ion C^{4+}), which may explain its low rate of diffusion. Further studies are required to clear out the forms of existence of oxygen in liquid iron. It is known at present that oxygen forms an interstitial solution in an elementary cell. With solidification of steel, oxygen separates in large amounts, so that it is practically absent in the solid solution and is found in steel only in combination with other elements (in the form of non-metallic inclusions).

Hydrogen and Nitrogen in Iron. It has been found experimentally that the solubility of hydrogen (and nitrogen) in iron at a given temperature is proportional to the square root of the partial pressure of hydrogen (or nitrogen) in the gaseous phase being in equilibrium with iron. It then follows that hydrogen (or nitrogen) dissolves in iron in atomic form. If hydrogen (or nitrogen) dissolved in the form of molecules, its solubility would be determined by the partial pressure of hydrogen (nitrogen) in the gaseous phase. The concentration of hydrogen in iron is calculated as mass percentage or in cm³ per 100 g of the metal, the relationship between these two values being given by the equation

$$[\mathrm{H}]\,\% = 0.89 \times 10^{-4}\,[\mathrm{H}]\ \mathrm{cm^3/100\ g}$$

The concentration of nitrogen is calculated as percentage of the mass of the metal.

In molten iron, hydrogen and nitrogen exist in elementary forms, rather than as hydrides or nitrides. At a temperature of 1600°C and a pressure P_{H_2} of 1 at, the solubility of hydrogen is 0.0027 per cent, i.e., there is one atom of hydrogen per 610 atoms of iron. The solubility of hydrogen in iron increases with temperature. It should be noted that the solubility of hydrogen in hydride-forming metals (Ti, Zr, Nb, Th, etc.) reduces with increasing temperature. The solubility of nitrogen in iron at 1600°C and $P_{N_2} = 1$ at is 0.039 per cent and increases with a further increase of temperature (see Fig. 138).

The coefficient of diffusion of nitrogen D_N in liquid iron at 1600°C is 3.8×10^{-5} cm²/s, i.e., slightly higher than that of carbon ($D_C = 3.2 \times 10^{-5}$ cm²/s). The diffusion coefficient of hydrogen is $D_H = (0.9\text{-}8.0) \times 10^{-3}$ cm² /s. Nitrogen and hydrogen form interstitial solutions with iron and are surface-active elements in liquid iron, but nitrogen loses its surface activity in the presence of nitride forming elements, such as titanium or chromium.

The research results given above are still insufficient to answer the question what are the forms of existence of all the above-mentioned impurities in liquid iron.

As regards the question of the location of impurities in an elementary solid crystal lattice, it can be answered with more certainty and confirmed from the standpoint of physical metallurgy. Imagine that an impurity is implanted into a lattice having a geometrically regular location of atoms of the main medium, i.e., new atoms with a different number of electrons and different structure appear in an elementary cell. If a substitutional solution is being formed, these "foreign" atoms will occupy the places of the atoms of the main element. New forces of interatomic interaction are formed in a given node, so that the state of equilibrium of the cell is disturbed.

For a new equilibrium to be established, the atoms must be displaced relative to their former regular positions as is determined by the new interatomic forces that have arisen through the intrusion of the impurity atom into the lattice. The positions of the atoms of the main medium will be changed. But as soon as this occurs and the atom occupies a new position, the equilibrium of the nearest atom in the node of a neighbouring lattice will be immediately disturbed. Then, the equilibrium in a further lattice will also be disturbed, and so on. Thus, the positions of atoms in crystal lattices will be altered in many atomic rows. The atoms at the nodes of the lattices of the main metal will be displaced in all directions in the cells near the one in which the initial atomic displacement in the cell node has occurred. The number of atomic layers involved in this disturbance will depend on the relative diameter of the impurity atom, the number of electrons, and the diameter of the atom of the main element. This means that an impurity atom implanted into the cell of an elementary lattice can disturb regular positions of thousands or even tens of thousands of atoms of the main metal. The resultant stresses cause a variation in the properties of the metallic body. The greater the concentration of impurity atoms, the more the substitutional solid solution structure distorts, and the more the properties of the metal change.

With the formation of solid interstitial solutions, the distortions of the structure are still greater than with solid substitutional solutions. As has been indicated by N. T. Gudtsov, atoms of the elements forming interstitial solutions are disposed so that the phenomenon of "selective" solubility occurs, i.e., if some impurity atoms have been introduced in a given place between the atoms of the main medium, the atoms of any other impurity will be uncapable of penetrating into that place of the interstitial solid solution.

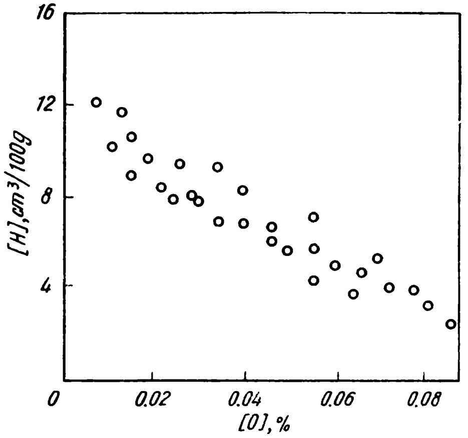

Fig. 6. Effect of oxygen content on dissolution of hydrogen in liquid iron

This circumstance requires special attention. If atoms of an impurity are disposed between iron atoms in a given place of the crystal lattice, it will be impossible, without complications, for the atoms of other elements capable of forming interstitial solid solutions to dispose in that place. Atoms of sulphur, oxygen and other elements possessing this property, cannot be now arranged, without special complications, in the voids between iron atoms, since these "voids" of the elementary lattice are already occupied by the atoms of another impurity. Figure 6 shows the effect of the content where n_1 and n_2 = numbers of moles of the first and second components, respectively

The number of moles of a given component is determined by the ratio of its mass in the solution to the molecular mass. Let us calculate, for instance, the molar proportions of the components of a solution by their mass percentages for a melt containing 45 per cent Si and 55 per cent Fe. The number of moles of the components in 100 g of the melt will be:

$$n_{Si}=\frac{45}{28}; \quad n_{Fe}=\frac{55}{55.84}$$

The molar proportion of silicon is

$$N_{Si}=\frac{n_{Si}}{n_{Si}+n_{Fe}}=\frac{\frac{45}{28}}{\frac{45}{28}+\frac{55}{55.84}}=0.62$$

and that of iron is

$$N_{Fe}=\frac{n_{Fe}}{n_{Si}+n_{Fe}}=\frac{\frac{55}{55.84}}{\frac{45}{28}+\frac{55}{55.84}}=0.38$$

Components are the substances (pure metals, elements or stable compounds) that form a system. In the physical metallurgy, components are understood as the elements (metals and non-metals) that form a melt.

Three phases, i.e., metallic, slag and gaseous, are distinguished in steelmaking. Each of them is homogeneous, separated from other phases by an interface, and has its own physical properties. In equations of chemical reactions, these phases are conditionally shown by taking the chemical symbols in brackets of different shapes: square brackets for the metallic phase, round brackets for the slag phase, and braces for the gaseous phase. For instance, [Mn], (MnO), and {CO} respectively denote manganese in the metallic phase, manganese oxide in the slag phase, and carbon monoxide in the gaseous phase.

The rate of a reaction depends on the rate of transport of the substances into the reaction zone, the rate of removal of reaction products, and viscosity of the interacting phases. The rate of a reaction increases with temperature since the viscosity then reduces and the rate of transport of substances increases. The conditions of equilibrium of physico-chemical processes also depend on temperature. For a reaction to end more rapidly, we have to know the effect of temperature on the reaction rate and the conditions of mobile equilibrium between the phases.

PHYSICO-CHEMICAL EQUILIBRIUM

When studying physico-chemical processes, their laws are derived by assuming, in the analysis, that the system is ideal. Thus, for instance, for an ideal gas, we neglect the action of intermolecular forces and the volume of the molecules themselves compared with the volume occupied by the gas; for an ideal solution, we assume that the chemical and physical properties of the substances forming it are similar. With these initial assumptions, the equations of physico-chemical equilibrium become simple, but they are applicable only to strongly rarefied gases and strongly diluted solutions, i.e., to systems whose properties are close to the properties of an ideal system.

When applying the laws derived for the ideal state to real systems, we introduce corrections, in particular by substituting the concentrations and partial pressures in the equilibrium equations respectively by the activities a and gas volatilities f. Numerical values of activity and volatility are found by multiplying concentrations and partial pressures by a correction factor, which is termed the activity coefficient γ; it characterizes the degree of deviation of the properties of the component considered in a real system from its properties in the ideal system: $a_i = c_i\gamma_i$ and $f_i = p_i\gamma_i$.

The activity coefficients for the components of ideal systems are taken equal to unity. In real systems, the activity coefficient may be either greater or smaller than unity. For instance, Table 1 gives the activity coefficients for carbon and oxygen dissolved in liquid iron at the temperature of steelmaking. As will be seen, the activity coefficients for carbon are very close to unity at a carbon concentration from 0 to 1.5 per cent and differ noticeably from unity at larger concentrations. The activity coefficient for oxygen is close to unity only for a very diluted solution and deviates appreciably from unity beginning with the concentration of 0.1 per cent C in the solution.

Table 1

Activity Coefficients for Carbon and Oxygen Dissolved in Liquid Iron at Steelmaking Temperature

C, %	γ_C	γ_O	$\gamma_C\gamma_O$	C, %	γ_C	γ_O	$\gamma_C\gamma_O$
0.0	1.00	1.00	1.00	0.5	1.00	0.67	0.67
0.1	1.00	0.93	0.93	1.0	1.03	0.50	0.515
0.2	1.00	0.86	0.86	1.5	1.08	0.42	0.454
0.3	1.00	0.79	0.79	2.0	1.23	0.39	0.48

The activities, as concentrations, are expressed in molar proportions (a_i) or as mass percentages (a_i,%). The activity coefficients of a substance have different values depending on whether the concentration is given in molar proportions $\left(\gamma_{i,N} = \frac{a_i}{N_i}\right)$ or in per cent by mass $\left(\gamma_{i,\%} = \frac{a_{i,\%}}{\% i}\right)$. For simplicity, the subscripts N and % to γ are omitted in further discussion, since it will be assumed in all cases that the value of γ corresponds to the respective units of concentration: $a_i = \gamma_i N_i$; $a_{i,\%} = \gamma_i \% i$.

The activity coefficient is taken equal to unity if the concentration of a solute is infinitesimal or the solvent contains no substance dissolved in it.

Given below are formulations of some of the laws of physico-chemical equilibrium for ideal and real systems.

THE LAW OF MASS ACTION

It is invariably found in experiments that the rates of chemical reactions are proportional to the concentrations of reacting substances. For a reversible chemical reaction between substances A and B, with the formation of substances C and D, i.e.

$$A + B \rightleftarrows C + D$$

the rates of the direct and reverse reactions are determined by the product of the concentrations of the substances reacting in the direct reaction and the product of the concentration of the substances obtained by the reverse reaction:

for the direct reaction

$$v_1 = K_1 C_A C_B$$

for the reverse reaction

$$v_2 = K_2 C_C C_D$$

where K_1 and K_2 = constants of the rate of direct and reverse reactions respectively, which depend on the nature of the initial substances, the products of reaction, and temperature

As the reaction proceeds, the concentrations of substances A and B decrease, and those of reaction products C and D, increase, owing to which the rate of the reverse reaction is increasing. Reversible reactions do not proceed to full exhaustion of even one of the reacting substances, but are finished when an equilibrium is established.

The equilibrium of a reaction is a state at which the rate of the direct reaction becomes equal to that of the reverse reaction. The state of equilibrium can exist until the conditions of the reaction (concentrations of substances, temperature, or pressure) are changed.

Therefore, at equilibrium ($v_1 = v_2$) we have

$$K_1 C_A C_B = K_2 C_C C_D$$

or

$$\frac{K_1}{K_2} = \frac{C_C C_D}{C_A C_B} = K$$

K being the equilibrium constant of the reaction.

Since the reaction rate constants K_1 and K_2 are invariable at a given constant temperature, then K is also a constant at that temperature.

If the concentrations of the initial substances C_A and C_B are designated respectively as L and S, and the concentrations of the reaction products C_C and C_D as W and R, then the equation of equilibrium can be written as follows:

$$K=\frac{WR}{LS}$$

In many chemical reactions, a number of molecules of substances A and B may participate. Their reactions are then written as

$$mA+nB \rightleftarrows pC+qD$$

and the equilibrium constant of this reaction is found from the relationship

$$K=\frac{W^pR^q}{L^mS^n}$$

or, for real systems

$$K=\frac{a_W^p a_R^q}{a_L^m a_S^n}$$

This equation expresses the law of mass action, which may be formulated as follows: at equilibrium of a reaction, the ratio between the product of the concentrations of the reaction products raised to the powers corresponding to their stoichiometric coefficients and the product of the concentrations of the initial substances raised to the powers corresponding to their stoichiometric coefficients is a constant at a given temperature.

If a reaction occurs between substances in the gaseous phase, the concentrations in the equilibrium equation are replaced by partial pressures*, since the concentration of a substance in the gaseous phase is proportional to the partial pressure of the substance.

For instance, for the reaction $2CO + O_2 \rightleftarrows 2CO_2$, its equilibrium constant is

$$K=\frac{\{CO_2^2\}}{\{CO\}^2[O_2]}$$

The concentrations of gaseous substances are usually replaced by their partial pressures, so that the equilibrium constant may be written as follows:

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* The partial pressure of a gas in a gas mixture is the pressure this gas would exert if it occupied the whole volume of the mixture at the same temperature. According to Dalton's law, the total pressure of a gas mixture is the sum of the partial pressures of its components.

$$K_p = \frac{p^2_{CO_2}}{p^2_{CO} p_{O_2}}$$

where p_{CO_2}, p_{CO}, p_{O_2} = partial pressures of carbon dioxide, carbon monoxide and oxygen in the mixture at equilibrium

With a constant pressure, the equilibrium constant of a reaction uniquely depends on temperature and can be expressed by the equation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

where ΔH = variation of the enthalpy of the system caused by the reaction; it is equal in magnitude to the thermal effect of the reaction, but opposite in sign (a positive thermal effect implies that the system absorbs heat, i.e., the reaction is endothermic)

R = 1.987 cal/°C = universal gas constant

T = absolute temperature, °K

The dependence of the equilibrium constant ln K on temperature T is shown graphically in Fig. 7. As will be seen, with an increase of temperature the constant for exothermic reactions reduces and that for endothermic ones, increases, i.e., exothermic reactions proceed more intensely at lower temperatures, while endothermic ones, at increased temperatures. Indeed, the exothermic reactions of oxidation of impurities Mn, Si, and P in iron occur rather rapidly at relatively low temperatures, while endothermic reactions, for instance, the reactions of reduction of silicon and manganese in an acid open-hearth furnace, can proceed only at a very high temperature. For that reason the effect of temperature on the equilibrium

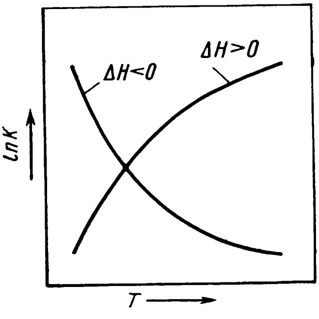


Fig. 7. Dependence of equilibrium constant on temperature

constant of a reaction is a particular case of the principle of mobile equilibrium, which is widely known in theoretical metallurgy as Le Chatelier's principle, formulated as follows: a change in any of the conditions of the true (stable) equilibrium of a system, such as temperature, pressure, or concentration, will shift the equilibrium in the direction of the reaction opposing the change.

This principle is used for qualitative estimation of the course of reactions, but is only applicable for systems near their equilibrium.

THE DISTRIBUTION LAW

If a system composed of two immiscible liquid phases has a substance, added to it, readily soluble in both phases, the substance distributes between them according to the distribution law, which states as follows: at equilibrium, the ratio of the concentrations (or activities) of a substance dissolved in two contacting immiscible phases is a constant at a given temperature:

$$L=\frac{(M)}{[M]}=\frac{a_{(M)}}{a_{[M]}}$$

where L = constant or coefficient of distribution of substance M between phases

(M) and $a_{(M)}$ = concentration and activity of the substance in slag

[M] and $a_{[M]}$ = concentration and activity of the substance in metal

In steelmaking, the distribution law is the basis for purification of steel from sulphur, phosphorus, and oxygen. For instance, critical grades of special high-quality steels are made by using the method of diffusion deoxidation, consisting in that the slag is covered with a deoxidizing mixture composed of foundry sand, ground ferro-silicon, breeze coke, and aluminium powder. These materials enter into the following reactions with ferrous oxide of the slag:

$$3(FeO)+2Al=(Al_2O_3)+3[Fe]$$

$$2(FeO)+Si=(SiO_2)+2[Fe]$$

$$(FeO)+C=\{CO\}+[Fe]$$

Since ferrous oxide is readily soluble in both slag and metal, the distribution law is applicable in this case

$$L_{FeO} = \frac{(FeO)}{[FeO]}$$

or, for real systems

$$L_{FeO} = \frac{a_{(FeO)}}{a_{[O]}}$$

where L_{FeO} = coefficient of distribution of oxygen between slag and metal

(FeO), $a_{(FeO)}$ = concentration and activity of ferrous oxide in slag

[FeO], $a_{[O]}$ = concentration and activity of oxygen in metal

Since the distribution coefficient L_{FeO} is a constant at a given temperature, oxygen begins to pass from the metallic phase into the slag phase owing to a decrease in the content of ferrous oxide in the slag caused by the deoxidizing action of silicon, coke, and aluminium. This process continues until the coefficient of distribution of FeO between the slag and metal, corresponding to a given temperature, is established. By adding a new portion of the deoxidizing mixture, a deeper deoxidation of steel can be attained.

THE HENRY LAW

Henry's law expresses the equilibrium condition of dissolution of a gas in a condensed (liquid or solid) phase. It states that the concentration of a gas in a solution at equilibrium is proportional to the partial pressure of the gas above the solution, i.e.

$$\frac{C}{p} = L$$

where C = concentration of the gas in the condensed phase

p = partial pressure of the gas in the gaseous phase

L = constant at a given temperature

The partial pressures and concentrations entering this equation should relate to one and the same form of existence of matter. For instance, hydrogen dissolves in iron in atomic state, so that the equation of equilibrium of the process must be of the form

$$\frac{[C_H]}{p_H} = L_H$$

where $[C_H]$ = concentration of atomic hydrogen in iron
p_H = partial pressure of atomic hydrogen in the gaseous phase
L_H = equilibrium constant of solubility of the gas

The dependence of L on temperature can be given by

$$\frac{d \ln L}{dT} = \frac{\Delta H}{RT^2}$$

where ΔH = variation of the enthalpy of the system on dissolution of the gas in the condensed phase.

THE RAOULT LAW

Raoult's law states that the partial pressure of the vapour of a solution component above a solution at equilibrium at a given temperature is proportional to the molar concentration of that component in the solution, i.e.

$$p = p_0 N$$

or, for real systems

$$p = p_0 a$$

where p = partial pressure of vapours of the component above the solution
N = molar concentration of component in solution
p_0 = pressure of saturated vapour above pure component
a = activity of the component in the solution.

1. EQUATIONS OF PHYSICO-CHEMICAL EQUILIBRIUM IN STEELMAKING

Equilibrium equations for the systems encountered in steelmaking can be simplified if the essential features of these systems are taken into consideration. For instance, the activity of iron in a melt may be taken equal to unity, since the iron content is almost 100 per cent. Therefore, the molar concentration and activity coefficient of iron are also very close to unity ($a = N\gamma$); the volatilities of substances are taken equal to their partial pressures; the activities of the substances saturating a given phase are taken equal to unity for that phase, since the pressure of vapours of a substance saturating a solution (p_{sat}) at equilibrium is equal to the pressure of vapours of the pure substance (p_0) and therefore, in accordance with Raoult's law, the activity of the substance saturating the solution is: $a = p_{sat} : p_0 = 1$; the activities in equations are sometimes replaced by concentrations in mass per cent or molar concentrations.

Given below are some examples to explain how equilibrium equations are compiled under the assumptions given above.

1. For the reaction

$$[\mathrm{Si}] + 2[\mathrm{O}] = (\mathrm{SiO_2})$$

its constant will be written as

$$K_{\mathrm{Si}} = \frac{a_{\mathrm{SiO_2}}}{[a_{\mathrm{Si}}, \%][a_{\mathrm{O}}, \%]^2}$$

but since the products of the reaction are saturated with silica and since $a_{\mathrm{SiO_2}} = 1$, the equilibrium constant can be written as

$$K_{\mathrm{Si}} = \frac{1}{[\%\ \mathrm{Si}][\%\ \mathrm{O}]^2}$$

As has been found experimentally, K_{Si} is uniquely dependent on temperature

$$\log K_{\mathrm{Si}} = \frac{31{,}000}{T} - 12.15$$

2. For the reaction $[\mathrm{Mn}] + (\mathrm{FeO}) = (\mathrm{MnO}) + [\mathrm{Fe}]$, if the slag phase is composed only of FeO and MnO, the following equilibrium equation can be used

$$K_{\mathrm{Mn}} = \frac{(\%\ \mathrm{MnO})}{[\%\ \mathrm{Mn}](\%\mathrm{FeO})}$$

The constant K_{Mn} uniquely depends on temperature:

$$\log K_{Mn} = \frac{6440}{T} - 2.95$$

But for slags of more complicated composition this value will change with a variation of slag composition, so that K_{Mn} will not be constant at a given temperature. As has been found by experiments, it may be expressed by the equation

$$\log K'_{Mn} = \log \frac{(\%\ \mathrm{MnO})}{[\%\ \mathrm{MnO}](\%\ \mathrm{FeO})} = \frac{5920}{T} + 0.332 \times 10^{-3}T - 1.7B + 1.778B^2 - 3.026$$

where B = amount of free lime in the slag:

$$B = [(\%\ \mathrm{CaO}) - 0.93(\%\ \mathrm{SiO_2}) - 1.18(\%\ \mathrm{P_2O_5})] \times 0.01$$

K'_{Mn} is not an equilibrium constant, since it may vary with variations of the slag composition at the same temperature. Such values are termed equilibrium characteristics.

The equilibrium constants for heterogeneous reactions are often written in a combined form. For instance, for the reaction

$$(\mathrm{CaO}) + [\mathrm{FeS}] = (\mathrm{CaS}) + (\mathrm{FeO})$$

its constant is

$$K' = \frac{(\%\ \mathrm{CaS})(\%\ \mathrm{FeO})}{(\%\ \mathrm{CaO})[\%\ \mathrm{FeS}]}$$

but it may also be written as follows

$$K'' = \frac{N_{(\mathrm{CaS})}N_{(\mathrm{FeO})}}{N_{(\mathrm{CaO})}[\%\mathrm{FeS}]}$$

where the concentrations of the components of the slag are given in molar proportions, and those of the components dissolved in the metal, as mass percentages. When writing down equilibrium constants of reactions occurring at the boundary between phases, the following rule is used: the concentrations of the components which are practically soluble in one of the phases are considered for that phase only, while the concentrations of the components soluble in both the slag and metal are considered for any of the phases, this being in accordance with the distribution law.

3. For the reaction [C] + [O] = {CO}, the condition of equilibrium can be expressed by the equation

$$K_{\mathrm{C}} = \frac{p_{\mathrm{CO}}}{[a_{\mathrm{C}}, \%]\,[a_{\mathrm{O}}, \%]}$$

According to experimental data, K_{C} uniquely depends on temperature:

$$\log K_{\mathrm{C}} = \log \frac{p_{\mathrm{CO}}}{[a_{\mathrm{C}}, \%]\,[a_{\mathrm{O}}, \%]} = \frac{1860}{T} + 1.643$$

Since we may write that

$$[a_{\mathrm{C}}, \%] = [\%\ \mathrm{C}]\,\gamma_{\mathrm{C}}$$

$$[a_{\mathrm{O}}, \%] = [\%\ \mathrm{O}]\,\gamma_{\mathrm{O}}$$

then the equilibrium equation of the reaction considered, in mass per cent, will be as follows:

$$\log K'_{\mathrm{C}} = \log \frac{p_{\mathrm{CO}}}{[\%\ \mathrm{C}]\,[\%\ \mathrm{O}]} = \frac{1860}{T} + 1.643 + \log (\gamma_{\mathrm{C}}\gamma_{\mathrm{O}})$$

But K'_{C} is no more a unique function of temperature, since the product of the activities of carbon and oxygen varies depending on carbon content (see Table 1). For that reason, and, as distinct from K_{C}, K'_{C} is called the equilibrium characteristic.

RELATIONSHIPS BETWEEN THE PRINCIPAL THERMODYNAMIC FUNCTIONS

Thermodynamics uses such concepts as internal energy U, enthalpy H, entropy S, isochoric potential F, isobaric-isothermal potential Z, which are unique continuous functions of state parameters (temperature, concentration, and pressure). The main peculiarity of these characteristics is that their variations in a process are independent of the path, speed, and kind of interaction, but are determined only by the initial and final states of the system.

The total energy stored in a substance is termed its internal energy U. All substances possess internal energy. The internal energy of a substance can vary during state transformations or chemical reactions. It either increases when energy is supplied from the outside, or decreases when part of the own energy of the substance passes to the surroundings as heat or work. The internal energy is usually related to one gram-molecule and measured in calories. If the internal energy of a system was U_1 in its initial state and has become U_2 in the final state, the magnitude $\Delta U = U_2 - U_1$ is termed the change of internal energy. The difference ΔU is considered positive if the energy of the reaction products is greater than that of the initial substances, i.e., if the internal energy increases in the process.

The processes occurring at a constant pressure may be conveniently characterized by a function called the enthalpy (heat content) of a system:

$$H = U + pV \tag{a}$$

where p = pressure and V = volume.

For solids and liquids at a small pressure, pV is negligible, so that the enthalpy is practically equal to the internal energy. A change of enthalpy is equal in magnitude to the thermal effect of a process, but is of the opposite sign.

Variations of internal energy in reactions are accompanied with either evolution or absorption of heat. The thermal effect of a reaction is usually related to a certain number of moles of the substances participating in the reaction. If a reaction occurs with evolution of heat, its thermal effect is considered positive and the reaction is called exothermic ($+Q_r$), i.e., the variation of the enthalpy of the system is negative: $\Delta H < 0$. But, if a reaction absorbs heat, its thermal effect is considered negative and the reaction is termed endothermic ($-Q_r$), i.e., the variation of the enthalpy of the system is positive: $\Delta H > 0$. Thus, the following relationship can be written:

$$+Q_r = -\Delta H; \quad -Q_r = +\Delta H \tag{b}$$

As follows from Hess' law, the thermal effect of a chemical transformation is independent of the sequence of the reaction, but depends only on the initial and final state of the system.

FREE AND BOUND ENERGY. ENTROPY

According to the second law of thermodynamics, internal energy cannot be fully transformed into work. The portion of the internal energy which cannot be transformed into useful work at a constant temperature is termed the bound energy. It is the product of the absolute temperature T and entropy S, i.e., $G = TS$.

Another portion of the internal energy, which is transformed into useful work at a constant temperature, is called the free energy and denoted by F. Hence

$$F = U - G \quad \text{or} \quad U = F + G \qquad (b)$$

To explain the concept of entropy, which is a function of the state of a system, let us recall that part of the heat in thermal processes is dissipated irreversibly, i.e., heat cannot be fully transformed into another kind of energy. It is this phenomenon that has given birth to the concept of entropy. Consequently, entropy is the measure of dissipation or irreversibility of heat or the measure of energy depreciation.

With an increase of temperature, thermal motion of particles in a substance is intensified, and an increase of the entropy reflects the tendency to scattering and disordered location of particles in the system. For that reason, entropy is the measure of disordered state of a system. Entropy increases with heating and melting of solids, boiling of liquids, sublimation, etc., i.e., in processes where a substance is transformed from a state of a lower energy to the state of a greater energy. Entropy also increases with expansion of gases in vacuum, dissolution of crystals in liquids, during chemical interactions leading to an increase of the volume, and dissociation of compounds, owing to the growth of the number of particles in the system. It also increases in processes resulting in the formation of molecules or gaseous compounds of a more complicated composition (for instance, $S_{O_3} > S_{O_2} > S_O$ or $S_{SO_3} > S_{SO_2} > S_{SO}$). This rule also holds true for liquids.

On the contrary, all processes that bring about the ordering of the system, i.e., cooling, solidification, compression, crystallization from solutions, and reactions resulting in a decrease of the volume, are accompanied by a reduction of their entropy.

Entropy is the measure of the probability of occurrence of a process in the system. All self-sustained processes, for instance, heat transfer from hot to cold bodies, expansion of gases in vacuum and some other most probable processes are attended with an increase of entropy. The unit of entropy is cal/mol·°C.

With a reversible process occurring in an isolated system, the entropy of the system remains unchanged. The work performed in such a process is maximum and exactly equal to the loss of free energy, i.e.

$$A_{\max} = \Delta F$$

With an irreversible process, the entropy of the system increases, and the work performed is less than the loss of free energy, i.e., $A < -\Delta F$.

The free energy of a system at a constant volume and temperature (the synonyms encountered in the specialist literature are: isochoric potential, isothermal potential at constant volume, isochoric-isothermal potential, useful energy, work function) is determined by the equation

$$F = U - TS$$

A change of the free energy is equal to the difference between the changes of the internal energy and bound energy

$$\Delta F = \Delta U - T\Delta S \qquad (c)$$

It then follows that the greater the change of the entropy of a system, the greater the free energy, i.e., the greater portion of the heat remains non-transformed into useful work.

In an irreversible process occurring at constant volume and temperature, the free energy decreases and becomes minimal at the moment of attaining the equilibrium. In a reversible process at constant volume and temperature, however, the free energy remains unchanged.

The function which determines the probable direction of a process in a system at constant temperature and pressure is termed the isobaric-isothermal potential (synonyms may be found in the literature: isobaric potential, thermodynamic potential, free energy of a system at constant pressure Gibbs' function or potential; apart from Z, it may be denoted by G, after Gibbs) and is determined by the equation

$$Z = H - TS$$

A change of the isobaric-isothermal potential is equal to the difference between the change of enthalpy and the change of free energy of the system, i.e.

$$\Delta Z = \Delta H - T\Delta S \qquad \text{(b)}$$

In an irreversible process occurring at constant pressure and temperature, the isobaric-isothermal potential decreases and becomes minimal at the moment of attaining the equilibrium. In a reversible process at constant pressure and temperature, the isobaric-isothermal potential remains unchanged.

Thus, a change of the isobaric-isothermal potential of a system is the principal criterion for the probability of a process to occur and the measure of the chemical affinity of the substances involved in the reaction. A process is probable if $\Delta Z < 0$ and improbable if $\Delta Z > 0$; at $\Delta Z = 0$ the system is in a mobile equilibrium.

The unit of isobaric-isothermal potential is cal/mol·°C. The principal relationships between thermodynamic functions are shown in Fig. 8.

The isobaric-isothermal potential can also be written as

$$Z = U - TS + pV = F + pV$$

Since, as has been given earlier, a change of enthalpy is equal in magnitude to the thermal effect, but has the opposite sign, we can write by using equation (*d*) that

$$\Delta Z = -(Q_r + T\Delta S)$$

This equation is usually employed to calculate equilibrium constants of reactions. The entropies of many substances involved in metallurgical reactions have been computed. A change of entropy ΔS in a reaction is found by subtracting the sum of the entropies of the initial substances from the sum of the entropies of the reaction products. A similar method is used to calculate ΔZ.

For certain reactions of steelmaking processes, the numerical values of equilibrium constants or characteristics are found experimentally.

For this purpose, the system under study is brought to equilibrium, with simultaneously measuring its temperature and determining (by sampling) the concentrations and partial pressures of the substances involved in the reaction. The data obtained are used to determine the dependence of the sought-for equilibrium ratio of the components on temperature, or, if this ratio is not constant at a given constant temperature, on the composition of reacting phases.

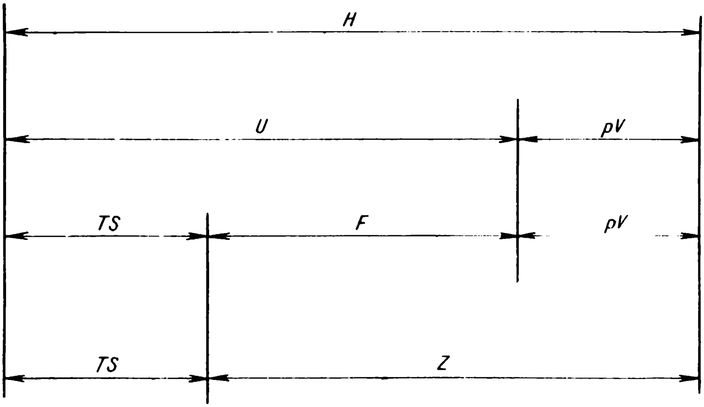


Fig. 8. Relationships between the principal thermodynamic functions

For a number of reactions their equilibrium constants are found by calculations because of the complexity of experiments. It is then expedient to use the value of ΔZ for the standard state of substances involved in a reaction, i.e. when they are under the same conditions.

The standard state of a substance is assumed to be the one which is stable under given conditions (p, T), usually at a pressure of 1 at and, for dissolved substances, at a concentration of unity. The standard state is related to the temperature of 25°C and the respective thermodynamic functions are denoted Z^0, G^0, etc.

As is known from physical chemistry, many reactions between ions, atoms and molecules in simple-structure liquids occur with the same rate as in a gaseous medium. This is an indication that the majority of the reactions occurring in steelmaking processes have very large rate constants and therefore may proceed rapidly. This is true both for homogeneous and heterogeneous reactions.

Reaction rate constants depend both on the nature of reacting substances and temperature. Thus, if a reaction occurs at a moderate temperature, a further increase of temperature by 10°C can increase the rate of the reaction 2-4 times, which is due to reaction rates' increase with temperature (in the region of high temperatures, reaction rates increase less rapidly). On the other hand, the rate of the processes of oxidation and reduction common in steelmaking are not very high. This may be explained by the fact that these processes are controlled not by the rates of the reactions proper, but the speed of supply of the reacting substances into the reaction zone and the speed of removal of the reaction products therefrom, i.e. depend on their diffusion stages.

Let us consider, by way of example, the reaction of carbon oxidation in Bessemer and open-hearth processes. In a Bessemer converter, where oxygen is intensively supplied to the reaction zone and the convective diffusion is many times the molecular diffusion owing to vigorous intermixing, and where surface phenomena are very effective, the rate of carbon oxidation reaches 0.3-0.5% per minute, whereas in an open-hearth furnace it is only 0.006-0.009% per minute because of poor supply of substances into the reaction zone under common conditions (when the process is not intensified with oxygen blowing).

Let us proceed with the analysis of the reaction by assuming its rate constant to be very large

$$A+B=C+D \qquad (e)$$

The concentration of the substances in the course of the reaction will be called actual (and denoted by a superscript A).

The rate of the reaction being analysed will be

$$v=K_1N_A^AN_B^A-K_2N_C^AN_D^A$$

Dividing the right- and left-hand parts of this equation by $K_2 N_A^A N_B^A$, we get

$$\frac{v}{K_2 N_A^A N_B^A} = \frac{K_1}{K_2} - \frac{N_C^A N_D^A}{N_A^A N_B^A} = K - \frac{N_C^A N_D^A}{N_A^A N_B^A}$$

where K = equilibrium constant of reaction (*e*).

It follows from this equation that the greater K_2 at a given rate v, the less will be the difference between the ratios of equilibrium concentrations and actual concentrations which ensure an appropriate rate of the reactions. Noting that the rates of oxidation-reduction processes in steelmaking are not very high, while the rate constants of most of the reactions are high, the majority of the reactions in steelmaking processes should be regarded to be in a near-equilibrium state provided that the metal is covered with slag. This conclusion has been confirmed by experimental data. Consequently, in studies of individual reactions of steelmaking, the laws of equilibrium are in many cases applicable even when the process is not at equilibrium and is accompanied by oxidation or reduction of the elements.

If the ratio of the actual concentrations

$$\frac{N_C^A N_D^A}{N_A^A N_B^A}$$

is denoted by K^A to distinguish it from the equilibrium constant, then the difference ($K - K^A$) will be related to a change of the isobaric potential in the reaction by the equation of an isotherm

$$\Delta Z = -RT(\ln K - \ln K^A)$$

or

$$\Delta Z = -4.575(\log K - \log K^A)$$

where R = gas constant, equal to 1.987 cal/°K·mol
4.575 = R multiplied by 2.303 (factor relating common logarithms with natural logarithms)

As indicated earlier, when calculating equilibrium constants, the substances involved in reactions are assumed to be in a standard state, i.e., with their partial pressures and concentrations equal to unity. Then K^A becomes equal to zero, since $\log K^A = \log 1 = 0$. The equations given above will then take the forms

$$\Delta Z^\circ = -RT\ln K = -4.575T\log K$$

whence

$$\log K = -\frac{\Delta Z^\circ}{4.575T} \qquad (f)$$

where ΔZ° = change of isobaric potential at a standard state of the substances involved in the reaction.

Substituting $\Delta Z = \Delta H - T\Delta S$ from equation (*d*) into equation (*f*), we get

$$\log K = -\frac{\Delta H^\circ}{4.575T} + \frac{\Delta S^\circ}{4.575}$$

At temperatures of steelmaking processes (1300°-1700°C), ΔH° and ΔS° vary only insignificantly, so that their values are conditionally taken at a temperature of 1600°C (1873°K). The equation will then take the final form

$$\log K = -\frac{\Delta H^\circ_{1873}}{4.575T} + \frac{\Delta S^\circ_{1873}}{4.575}$$

Using the available data on ΔH° and ΔS° (Table 2), we can calculate the equation and final value of the temperature dependence for the equilibrium constant of a reaction. Other methods for determining equilibrium constants may also be used.

Let us consider an example of using ΔH° and ΔS° to calculate the equilibrium constant of the reaction

$$\{H_2\} + 1/2\,\{O_2\} = \{H_2O\}$$

We substitute ΔH° and ΔS° into the equation of the constant

$$\log K = -\frac{\Delta H^\circ_{1873}}{4.575T} + \frac{\Delta S^\circ_{1873}}{4.575} =$$

$$= -\frac{-60180}{4.575T} + \frac{-13.93}{4.575} = \frac{13150}{T} - 3.045$$

For reactions for which the values of ΔH° and ΔS° are not found in Table 2, an indirect method may be used, which essentially consists in combining the values ΔZ°

Table 2

Thermal Effects and Entropy Changes of Selected Reactions at Temperatures of Steelmaking

Reaction	$\Delta H°$, cal/mol	$\Delta S°$, cal/mol °C
Gaseous reactions		
$\{H_2\}+0.5\{O_2\}=\{H_2O\}$	— 60 180	—13.93
$\{CO\}+0.5\{O_2\}=\{CO_2\}$	— 66 560	—20.15
$C_{graphite}+0.5\{O_2\}=\{CO\}$	— 28 100	+20.20
$C_{graphite}+\{O_2\}=\{CO_2\}$	— 94 640	+ 0.05
$\{H_2\}+\{CO_2\}=\{H_2O\}+\{CO\}$	+ 6 380	+ 6.22
$C_{graphite}+\{CO_2\}=2\{CO\}$	+ 38 460	+40.35
$\{H_2\}+0.5\{S_2\}=\{H_2S\}$	— 21 680	—11.81
$0.5\{S_2\}+\{O_2\}=\{SO_2\}$	— 86 380	—17.30
$C_{graphite}+2\{H_2\}=\{CH_4\}$	— 21 960	—26.61
$2C_{graphite}+\{H_2\}=\{C_2H_2\}$	+ 53 200	+12.66
$\{H_2\}=2\{H\}$	+108 300	+28.80
Formation of oxides		
$Fe_l+0.5\{O_2\}=(FeO)_l$	— 56 830	—11.94
$Mn_l+0.5\{O_2\}=(MnO)_s$	— 97 000	—21.4
$MnO_s=MnO_l$	+ 10 700	+ 5.2
$\{Mg\}+0.5\{O_2\}=(MgO)_s$	—176 500	—47.5
$\{Ca\}+0.5\{O_2\}=(CaO)_s$	—192 000	—49.1
$2Al_l+3/2\{O_2\}=(Al_2O_3)_s$	—400 000	—76.6
$2Cr_s+3/2\{O_2\}=(Cr_2O_3)_s$	—265 050	—60.4
$2V_s+3/2\{O_2\}=(V_2O_3)_s$	—287 300	—54.3
$Si_l+\{O_2\}=(SiO_2)_s$	—217 700	—47.0
$Ti_s+\{O_2\}=(TiO_2)_s$	—217 600	—41.9
$Zr+\{O_2\}=(ZrO_2)_s$	—256 000	—44.0
$Mo_s+\{O_2\}=(MoO_2)_s$	—137 000	—39.4
$W_s+\{O_2\}=WO_{2s}$	—139 150	—41.7
Formation of sulphides		
$Fe_l+0.5\{SO_2\}=FeS_l$	— 34 000	—10.4
$Mn_l+0.5\{S_2\}=MnS_s$	— 68 700	—19.1
$\{Mg\}+0.5\{S_2\}=MgS_s$	—132 300	—45.7
$\{Ca\}+0.5\{S_2\}=CaS_s$	—169 600	—47.4
$2Al_l+3/2\{S_2\}=Al_2S_{3s}$	— 16 440	—69.0

Table 2 (continued)

Reaction	$\Delta H°$, cal/mol	$\Delta S°$, cal/mol °C
Formation of nitrides		
$B_s+0.5\{N_2\}=BN$	− 27 700	−10.4
$Al_l+0.5\{N_2\}=AlN_s$	− 62 300	−30.1
$Ti_s+0.5\{N_2\}=TiN_s$	− 80 300	−20.1
$V_s+0.5\{N_2\}=VN_s$	− 43 000	−21.4
$Zr+0.5\{N_2\}=ZrN_s$	− 82 200	−22.0
$3Si_l+2\{N_2\}=Si_3N_{4_s}$	−208 600	−97.2
Formation of carbides		
$\{Ca\}+2C_{graphite}=CaC_{2_s}$	−59 800	−21.6
$4Al_l+3C_{graphite}=Al_4C_{3_s}$	−35 700	−28.1
$Si_l+C_{graphite}=SiC_s$	−38 400	− 8.5
$Ti_s+C_{graphite}=TiC_s$	−57 300	− 2.5
Dissolution		
$Ni_l=[Ni]$	0	+ 9.21
$Mn_l=[Mn]$	0	+ 9.11
$Co_l=[Co]$	0	+ 9.26
$Cr_s=[Cr]$	+ 4 350	+11.11
$Mo_s=[Mo]$	+ 6 280	+12.32
$W_s=[W]$	+ 7 640	+13.62
$Si_l=[Si]$	−20 010	+ 7.46
$Cu_l=[Cu]$	+ 9 300	+ 9.40
$V_s=[V]$	− 3 900	+11.07
$Al_l=[Al]$	−11 700	+ 7.70
$Ti_s=[Ti]$	− 7 000	+11.00
$Zr_s=[Zr]$	− 7 000	+12.20
$C_{graphite}=[C]$	+ 8 900	+12.10
$0.5\{N_2\}=[N]$	+ 2 580	− 5.02
$0.5\{H_2\}=[H]$	+ 7 640	− 7.68
$0.5\{O_2\}=[O]$	−27 930	+ 0.57
$(FeO)=[O]+[Fe]$	+28 900	+12.51
$0.5\{S_2\}=[S]$	−31 520	− 5.27
$2\{CO\}=[C]+\{CO_2\}$	−29 950	−28.24
$\{H_2O\}=[O]+\{H_2\}$	+32 250	+14.50

Table 2 (continued)

Reaction	ΔH°, cal/mol	ΔS°, cal/mol °C
$\{H_2O\}=2[H]+[O]$	+ 47 530	− 0.86
$\{CO_2\}=[O]+\{CO\}$	+ 38 050	−20.72
$\{CO\}=[C]+[O]$	+ 8 510	− 7.52
$(MnO)=[Mn]+[O]$	+ 58 400	+25.98
$(SiO_2)=[Si]+2[O]$	+141 830	+55.60
$(Cr_2O_3)=2[Cr]+3[O]$	+189 960	+84.33
$(V_2O_3)=2[V]+3[O]$	+196 600	+78.18
$\{H_2S\}=[S]+\{H_2\}$	− 9 840	+ 6.54
$\{SO_2\}=[S]+2[O]$	− 1 340	+12.81

of reactions by adding or subtracting them algebraically. A change of ΔZ of a reaction and also the thermal effect of the reaction depend only on the initial and final state, but not on the sequence of the reaction. This makes it possible to find the value of ΔZ of a combined reaction by the values of ΔZ of its composite reactions, treating these as common algebraic expressions.

The equation of the isobaric potential is also applicable to dissolution of substances in melts, variations of the aggregate state, and other processes occurring with either absorption or evolution of heat.

INTENSITY OF OXIDATION OF ELEMENTS IN A STEELMAKING BATH

As has been indicated earlier, a standard change of the thermodynamic potential is a measure of chemical affinity of substances. With the formation of an oxide of an element, a change of the isobaric-isothermal potential characterizes the amount of useful work to be performed in order to separate the oxygen from the element ($A_{max} = -\Delta Z^0$). A higher negative value of $-\Delta Z$ corresponds to a stronger bond between oxygen and an element. Values of ΔZ for the reactions of oxide formation of various elements have been calculated and are shown in Fig. 9 (they have negative signs).

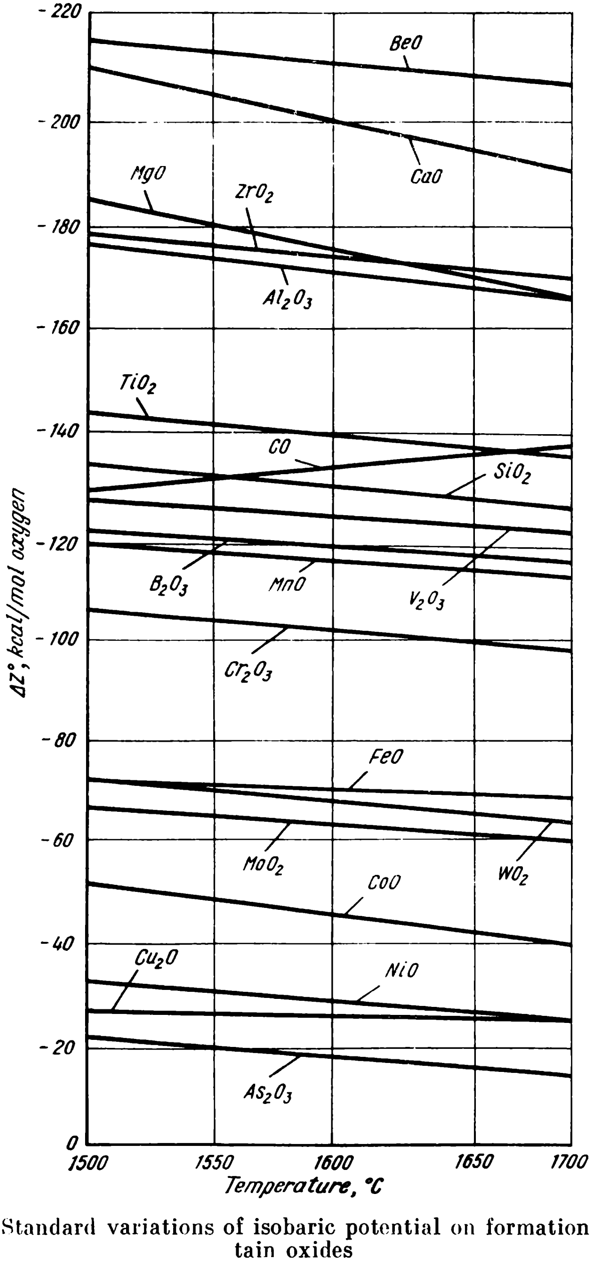


Fig. 9. Standard variations of isobaric potential on formation of certain oxides

By analysing the shape of the curves in Fig. 9, it may be seen that when oxygen is supplied at a given temperature and atmospheric pressure into the bath, it will react with all the elements present there, but with different intensities, depending on the concentration of the elements and their strength of bondage with oxygen, which is decided by ΔZ. For instance, at 1600°C the bond strength of the oxides of the following elements increases successively in the order of the elements: As, Cu, Ni, Co, Mo, W, Fe, Cr, Mn, B, V, Si, C, Ti, Al, Zr, Mg, Ca, and Be.

The predominant element in a steelmaking bath is iron. Let us see in Fig. 9 how the FeO line relates to the lines for other oxides. If, for instance, oxygen is supplied to the bath at a temperature of 1600°C and the bath contains, apart from iron, also elements whose oxides have a greater bond strength to oxygen, i.e., their lines are located above the FeO line, these elements react with the oxygen with greater intensity than iron does.

The oxides whose lines are below the FeO line are less stable and the elements forming these oxides (W, Mo, Co, Ni, Cu, As) obtain only a negligible part of the oxygen supplied to the bath. If we assume that this part of the oxygen is still capable of forming oxides of these elements, these will be decomposed, owing to their poor stability, by the elements whose lines lie above the lines of these elements.

Thus, the greater is the absolute negative value ΔZ of an oxide, with the greater intensity will be oxidized in the bath the element forming this oxide, i.e., the greater proportion of the oxygen supplied will fall on that element. A point of importance is that the absolute negative change of the isobaric potential for FeO must always be smaller than for other elements commonly present in the bath; this reduces the oxidation loss of iron.

For the same temperature and activity of ferrous oxide, the conditions of distribution of oxygen among the elements in the slag may vary substantially with variations of the activities of the oxides being formed. As a rule, the smaller the activity of an oxide in slag, the greater the intensity of oxidation in the bath of the element forming this oxide. Thus, for instance, basic slags contain large amounts of $(CaO)_2SiO_2$ and $(CaO)_4P_2O_5$ and only negligible amounts of free oxides SiO_2 and P_2O_5, which are formed owing to thermal dissociation. The activities of these free oxides are low and therefore silicon and phosphorus are oxidized in the basic process relatively rapidly and to a very large extent. On the contrary, in acid open-hearth slags, in which the content of SiO_2 is high and exceeds the saturation limit, the activity of SiO_2 is high. For that reason silicon is oxidized very slowly, its concentration in the bath never dropping below 0.05-0.08 per cent.

2. SURFACE PHENOMENA IN STEELMAKING

Surface phenomena at phase boundaries (gas phase, metal phase, slag phase, and refractories) play a very important part during melting of steel. It is then of value to recall some concepts relating to these phenomena.

SPECIFIC FREE SURFACE ENERGY

As the surface of a liquid increases, work is being done to overcome the forces of molecular cohesion, so that the free energy of the system grows. An increase of the free energy related to 1 cm^2 of the interface formed between the substance considered and any other phase (saturated vapours of the substance, air, etc.) is termed the specific free surface energy, σ (erg/cm^2). The concept of surface tension is sometimes used, which is understood as the forces directed tangentially over the surface of the body. When considering the surface phenomena at the boundary between two condensed phases, the term interphase tension is used.

The surface tension (dyne/cm) is the resultant of the forces of surface tension related to unit length.

The specific free surface energy of liquids depends on their composition and temperature. As distinct from the majority of metals, the specific free surface energy σ of iron and its alloys increases with temperature. Within the temperature range of steelmaking processes, however, the composition of molten metal and slag has the decisive effect on σ.

The magnitude of surface tension depends not only on the physical properties of the liquid, but also on the nature of the medium in contact with that liquid; this medium has a strong effect on the liquid particles in the contacting layer. For that reason the symbol σ is written with a subscript to indicate the boundary medium (g, s, sl, and m respectively for gas, solid surface, slag, and metal).

Among the impurities common in iron and its alloys, phosphorus, sulphur, and oxygen have the strongest effect on the specific free surface energy; with an increase of their concentration, $\sigma_{m\text{-}g}$ of a melt decreases. An increase of the carbon content in an iron melt also results in a reduction of $\sigma_{m\text{-}g}$, this effect being augmented in the presence of sulphur in the melt (Fig. 10).

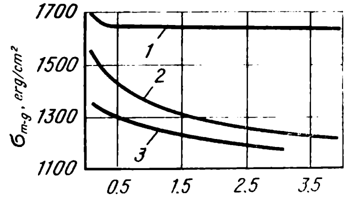


Fig. 10. Effect of carbon on specific free surface energy of iron melts containing sulphur *1*—0.035-0.070% C, 0.006% P, 0.004% S; *2*—carbonyl iron (0.03% S); *3*—0.09%C, 0.026% S, 0.025% P.

As has been found by numerous experiments, the values of specific free surface energy for liquid slags in contact with a gaseous phase are $\sigma_{sl\text{-}g} = 500\text{-}600$ erg/cm² for basic slags and $\sigma_{sl\text{-}g} = 300\text{-}400$ erg/cm² for acid slags. It has been established that $\sigma_{sl\text{-}g}$ in basic slags decreases as the content of MnO, SiO_2, P_2O_5, TiO_2, V_2O_5, FeO, Cr_2O_3, WO_3 is increased. The value of $\sigma_{sl\text{-}g}$ can also be reduced by lowering the content of CaF_2, CaO, MgO, Al_2O_3 in the slag. The interphase specific surface energy (interphase tension) at the metal-to-slag boundary, $\sigma_{m\text{-}sl}$, has not yet been studied sufficiently. According to Antonov's rule, the interphase tension at the boundary between two liquids is equal to the difference between the surface tensions of these phases at the boundary with a gas phase. This rule is probably valid if the two liquids are mutually fully wettable.

The magnitude of $\sigma_{m\text{-}g}$ depends on the concentration of impurities in steel, varying between 1100 and 1600 erg/cm²; it increases as the steel is refined from impurities.

The interphase energy near the solidification point of liquid steel (at the interface between solid crystals and still liquid metal) is approximately $\sigma_{m_l\text{-}m_s} = 20\text{-}40$ erg/cm², i.e., much smaller than the interphase tension between slag and metal.

The surface properties of slags determine their liability to foaming. This is observed both in oxygen-blown converters and open-hearth furnaces. The properties of slag also determine its capability of running off from the metal during boiling, which ensures a more intense passage of gases from the furnace atmosphere into the metal.

WETTING

If a small amount of liquid is poured onto a plane surface, the liquid will either form a droplet or spread over the surface, so that the surface tensions of the phases come to an equilibrium. As can be seen from the directions of the forces of surface tension at equilibrium (Fig. 11):

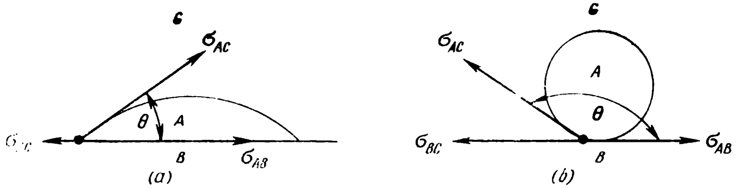


Fig. 11. Equilibrium of surface tension forces forming a droplet

$$\sigma_{BC} = \sigma_{AB} + \sigma_{AC} \cos \theta$$

where σ_{BC} = surface tension on boundary between phases *B* (the surface on which the liquid has been poured) and *C* (gas phase surrounding the droplet)

σ_{AB} = surface tension on boundary between phases *A* (the liquid that forms the droplet) and *B* (the surface on which the liquid has been poured)

σ_{AC} = surface tension on boundary between phases *A* and *C*

θ = wetting angle characterizing the spread of the liquid

It follows from the above equation that

$$\cos\theta = \frac{\sigma_{BC} - \sigma_{AB}}{\sigma_{AC}}$$

The wetting angle θ is independent of the size of droplet, but depends only on the nature of the interface. It may vary between 0 and 180°. When $\theta = 0$, phase B (the surface onto which the liquid has been poured) is fully wettable by phase A (the liquid), so that $\cos\theta = 1$ and

$$\sigma_{BC} - \sigma_{AB} = \sigma_{AC}$$

or

$$\sigma_{BC} = \sigma_{AC} + \sigma_{AB}$$

When $\theta = 180°$, liquid A is fully uncapable of wetting surface B, so that $\cos\theta = -1$ and

$$\sigma_{BC} - \sigma_{AB} = -\sigma_{AC}$$

or

$$\sigma_{BC} = \sigma_{AB} - \sigma_{AC}$$

In intermediate cases $(0 < \theta < 180°)$, partial wetting is observed between phases A and B, which is the greater, the closer to zero the angle θ is.

If the surface tension at a solid-gas boundary, σ_{BC}, is greater than that at the solid-liquid boundary, σ_{AB}, the solid will be wetted by a given liquid (Fig. 11*a*). The condition of wettability is determined by the inequality $\sigma_{BC} > \sigma_{AB}$, in which case $\cos\theta > 0$, i.e., the wetting angle is acute.

If the surface tension at a solid-liquid boundary, σ_{AB}, is greater than that at the solid-gas boundary, σ_{BC}, the liquid will not spread over the solid (Fig. 11*b*). This condition is expressed by the inequality $\sigma_{AB} > \sigma_{BC}$, with $\cos\theta < 0$, i.e., the wetting angle is obtuse.

The surface of the bath of an open-hearth furnace is rough because of numerous projections and recesses in the lining or fettling. Besides, there are micropores, fissures, and capillary passages between crystals of refractories. These portions of the surface of the hearth are decisive for the process of formation of bubbles of CO in the reaction of carbon oxidation.

The refractory lining of the bath, either basic or acid, is only poorly wettable with metal. As can be seen from the data of Table 3, even for slagged magnesite the wetting angle is higher than 90°, which is indicative of the fact that the surface of the bath has numerous pores, passages, recesses, etc., that are not filled with metal.

Table 3

Wetting Angles

Liquid	Solid surface being wetted	Temperature, °C	Wetting angle θ, degrees
Armco iron	Quartz	1530-1600	108-115
	Alumina	1530-1600	139
	Magnesite	1530-1600	126
	Magnesite, slagged with oxidizing slag	1530-1600	100-107
Carbonyl iron with 0.07% C	Alumina	1560	141
	Molten magnesia	1560	139
Commercial iron with 0.09% C and 0.09% Mn	Molten magnesia	1560	121
Oxidizing slag	Magnesite	1600	0
	Solid iron	1450-1520	55
	Liquid iron	1530-1560	90

The effect of roughness of the walls of a vessel has been shown in laboratory experiments on melting steel in glazed quartz crucibles. The boiling of the metal could not start until the glaze was removed in some places of the crucible by a glass stick, though the metal was quite saturated with oxygen (the value $m = [C]\,[O]$ in it was 10-15 times the equilibrium value).

ADHESION

Adhesion is the sticking between two contacting phases at their interface caused by intermolecular attraction forces. The amount of energy to be spent, for instance, to separate the slag from the metal at their interface of an area of 1 cm² is equal to the difference between the sum of the free surface energies of the metal and slag at their interfaces with the gas phase after their separation and the free surface interphase energy prior to their separation. The unit work of adhesion can be determined by the equation

$$W_{m\text{-}sl} = \sigma_{sl\text{-}g} + \sigma_{m\text{-}g} - \sigma_{m\text{-}sl}, \ \text{erg/cm}^2$$

Referring to Fig. 11 (where B is metal, A is slag, and C is gas), the equation can be re-written as

$$W_{m\text{-}sl} = \sigma_{AC} + \sigma_{BC} - \sigma_{AB}, \ \text{erg/cm}^2$$

Solving this equation together with the earlier equation of the equilibrium of surface tensions of a droplet

$$\sigma_{BC} = \sigma_{AB} + \sigma_{AC} \cos\theta$$

we obtain

$$W_{m\text{-}sl} = \sigma_{AC} + \sigma_{AB} + \sigma_{AC} \cos\theta - \sigma_{AB} = \\ = \sigma_{AC}\,(1 + \cos\theta_{AC}), \ \text{erg/cm}^2$$

Using this equation, let us approximately determine the energy required to separate slag from metal, i.e., the work of adhesion, for a basic slag (assuming $\sigma = 550$ erg/cm² and $\theta = 45°$):

$$W_{m\text{-}sl} = 550\,(1 + 0.707) = 935 \ \text{erg/cm}^2$$

and for an acid slag (assuming $\sigma = 350$ erg/cm² and $\theta = 45°$)

$$W_{m\text{-}sl} = 350\,(1 + 0.707) = 595 \ \text{erg/cm}^2$$

A moderate adhesion between slag and metal may be even desirable to diminish running-off of the slag from the surface of boiling metal; but an excessive adhesion, as, for instance, in electric-arc melting with carbide slags, can result in a strong sticking of slag to metal and therefore in contamination of the latter with slag inclusions. Such slags have a small wetting angle with metals (5-10°) and a low interphase tension (200-300 erg/cm^2). This is especially dangerous when melting quality steels, such as ball-bearing steel. The only measure for combating this undesirable property of slags is to convert a carbide slag into white slag by special process techniques.

Since slag is liable to stick to metal it is difficult to remove it completely with slagging-off during dephosphorization or desulphurization; either part of the slag is then left in the bath or metal is inevitably lost during the slagging-off.

Adhesion is also responsible, to some extent, for aggregation of non-metallic inclusions suspended in the metal and their assimilation by the slag. As has been indicated in the specialist literature, the less the adhesion between slag inclusions and metal, i.e., the greater the wetting angle between the metal and inclusions and the greater the tension of their interface, the more probable, from the thermodynamic viewpoint, is the aggregation of liquid slag inclusions in the metal.

Assimilation of the inclusions floating up from the metal to the metal-slag interface by the slag cover is also due to the surface properties of these inclusions. The greater the specific energy at the metal-inclusion interface and the greater the adhesion between the slag cover and inclusions, i.e., the lower the tension at the inclusion-slag cover interface, the easier the inclusions are absorbed and assimilated by the slag cover. On the contrary, if a slag cover is only poorly wettable with inclusions, it cannot assimilate them. In that case inclusions are repulsed from the lower surface of the slag cover as elastic balls and remain suspended in the surface layer of the metal. This phenomenon is observed, for instance, when melting steel in acid open-hearths by the silicon-reducing process with very thick low-manganese slags. In large open-hearth furnaces with a deep bath, a zone in which the metal is intermixed with slag may be formed owing to a low rate of carbon oxidation under the cover of slag. A thick slag cover cannot assimilate slag particles from that zone.

It should be noted that the above examples of the effect of the surface properties of various phases are only an indication that assimilation of inclusions by the slag cover is thermodynamically feasible. Kinetic processes that ensure removal of inclusions are, however, more critical here. They are not only related with surface phenomena, but also depend on the viscosity of the slag cover, intensity of intermixing of the phases, solubility of inclusions in the slag cover, mobility of molecules in the surface layer of the slag cover, the nature of ionic interactions at the inclusion-slag cover interface, etc.

COHESION

Cohesion is the sticking of neighbouring particles of a body under the action of intermolecular attraction forces. To break the body, an energy must be spent (cohesion work) to overcome these forces, since cohesion is characterized by the resistance of particles of liquid to the formation of a new interface. If a liquid column A one square centimetre in cross section is disrupted, two surfaces in contact with the gaseous phase will be formed, each of an area of 1 cm^2. The energy to be spent for the formation of each of these surfaces is σ_{AC}. Consequently, the work of cohesion for disruption of a liquid column into two parts is $2\sigma_{AC}$ erg/cm^2.

Cohesion work is performed in converter processes when the air or oxygen being supplied to a Bessemer converter disrupts the metal column into numerous droplets. This must be taken into account in theoretical calculations of converter processes.

REACTION RATES IN THE BATH

The rate of a reaction is determined by the change in the concentration of a reagent in unit time. In a homogeneous medium, it depends on the number of effective collisions per unit time of reacting particles possessing an energy equal to or exceeding the activation energy E. The number of collisions is likely to be proportional to the number of particles in unit volume of the reaction zone and therefore the rate of a reaction is always proportional to the product of the concentrations of the reacting substances.

High rates of interaction of reagents are due to mass transfer of substances and high temperatures of the process. With an increase of temperature, the proportion of the particles whose energy exceeds the activation energy rises too.

$$\frac{Z}{Z_0} = e^{\frac{-E}{KT}}$$

where Z = number of active collisions
Z_0 = total number of collisions
E = activation energy
T = temperature
$K = 1.3805 \times 10^{-16}$ erg/degree = Boltzmann's constant

The rate of a complex heterogeneous process (most reactions occurring in the steel bath are of this type), which usually consists of a number of stages, depends on the rate of its slowest stage, but not on the rate of the chemical reaction proper, which, as has been shown earlier, may proceed at a very high rate. Therefore, the rate of the process will be determined by the diffusion processes involving the supply of reagents to the reaction zone and removal of reaction products therefrom.

Mass transfer in liquids is due to molecular diffusion caused by thermal motion of molecules and convective diffusion caused by convective currents always existing in real liquids. The rate of molecular diffusion is usually very low because of the low value of the coefficient of molecular diffusion (10^{-4} cm^2/s at 1500°C).

The supply of reacting substances to the reaction zone and the removal of reaction products are largely dependent on convective diffusion, the area of the surface through which the supply and removal are effected, the viscosity of the phases of the process, and the resistance at the interphase boundaries. All these factors may favour the acceleration of the reaction.

A reaction can be accelerated even more if its phases are intermixed. Then turbulent diffusion becomes decisive for effective collisions of particles. The rate of turbulent diffusion is much greater than that of molecular diffusion.

In an open-hearth furnace, mass transfer is increased when the metallic bath is agitated by bubbles of carbon oxide. According to some reports, the turbulent diffusion can reach 82 cm^2/s, depending on the rate of carbon oxidation. Turbulent diffusion in converter processes is even higher, which is confirmed by greater rates of carbon oxidation in Bessemer converters (up to 0.5 % C/min) compared with the rates of carbon oxidation in open-hearth furnaces (0.008-0.010% C/min). This can be explained by the peculiarities of the converter process, in which the slag and metal are disintegrated; this increases many times the area of contact surface and activates surface phenomena. The penetration of the oxygen jets into the metal also increases many times the area of surface contact, which, together with bubbling of the bath caused by the blown-in oxygen and carbon oxide bubbles, accelerates mass transfer of the reacting substances and thus increases the rates of reactions.

Chapter Three

PRODUCTION AND CLASSIFICATION OF STEELS

STEEL PRODUCTION IN THE USSR

Archaeologic excavations on the USSR territory discovered numerous iron articles: labour implements, swords, arrows, lances, tools, etc., which are indicative of the fact that the history of steel manufacture in this country ascends to the hoary antiquity.

The Slav tribes that inhabited the southern districts of the country in the 7-8th centuries mastered the crafts of making metal articles and weapons. There are some evidence that the Slavs produced wrought iron and steel even before the 9th century. Casting of bronze bells and guns was started in the 14th century. Bloomery iron was made in small bloomery hearths. In the 15-16th centuries, iron-making crafts flourished in the central and northern areas of the country. In the 17th century, tens of works for producing pig iron, steel and wrought iron were built in the Urals and the central region, near Tula.

A special role in the development of iron and steel making in Russia belongs to the Russian tsar Peter the First, who is by right reputed one of the founders of Russian metallurgy. The development of iron- and steel-making in Russia was greatly favoured by the availability of pure rich iron ores in the Urals.

By gradually developing and improving the processes of iron- and steel-making, Russia became in the second half of the 18th century the main supplier of pig iron and steel to Western Europe, in particular, to Great Britain. A new upsurge in the development of iron- and steel-making was observed in the second half of the 19th century after new iron and steel works had been built in the south of the country.

In 1913, before World War I, Russia produced 4.3 mln tons of steel. The production of steel dropped sharply during the years of the war, and also during the intervention and Civil War. Thus, for instance, only 194,000 tons of steel was produced in 1920. During the period of reconstruction that followed, steel production was gradually raised and reached the pre-war level (around 4.25 mln t) in 1928.

In the period of industrialization, enormous work was done on reconstruction of existing and building of new iron and steel works. A second coal-iron base was founded in the east of the country. Progressive engineering and technology were introduced at the new iron and steel works and integrated works. Measures were taken to overcome the lag of the ferrous metallurgy in the rates of progress behind other branches of national economy, and especially the lag in the production of steel and rolled products as compared to the pig iron production. An enormous amount of work was done on training the specialists and skilled workers for iron and steel works. The result was that as much as 18.3 mln tons of steel was produced in 1940.

Steel production reduced somewhat during the Great Patriotic War, but was rapidly restored soon after the war and then grew at high rates as can be seen from the table:

Year	1945	1950	1955	1960	1965	1966	1967
Production, mln t	12.3	27.3	45.3	65.3	91.0	96.9	102.2
Year	1969	1970	1971	1972	1973	1974	1975
Production, mln t	110.0	116.0	121.7	126.0	131.0	136.0	141.0

Among the measures aimed at further development of steel manufacture in the country are: large intensification of steelmaking processes by application of new techniques, including pure-oxygen blasting; automation and complex mechanization of steelmaking processes; introduction of new large-capacity steelmaking plants; and further transfer of open-hearth furnaces to natural-gas firing. Oxygen-converter and electric processes of steelmaking will be developed especially rapidly. The progressive method of continuous casting of steel will find wider implementation.

CLASSIFICATION OF STEELS

Pig iron and steel are alloys of iron and carbon. They may additionally contain other elements, such as manganese, silicon, phosphorus, sulphur. In engineering, iron-carbon alloys are classed into iron, steel, and pig iron according to the carbon content in them; thus, technical iron contains 0.01-0.025 per cent C; steel, 0.025-2.06 per cent C; and pig iron, more than 2.06 per cent C.

Since steels are the main materials in construction and machine engineering, the requirements imposed on them are very diverse. In some structures, steel must be not only hard and strong, but also ductile. In others, it must possess a high wear resistance and at the same time be easily machinable. Steel is also used to make cutting tools capable of cutting other materials, including the steel the tool is made of. These diverse requirements are met by specially selecting the components of a steel and subjecting it to heat treatment.

Steels are classified by the method of manufacture, purpose, quality, and composition.

According to the method of manufacture, steels are classified as follows:

(a) converter steels, i.e., produced by the acid Bessemer, basic Bessemer or oxygen-converter process (various modifications);

(b) open-hearth steels, produced in acid or basic open-hearth furnaces;

(c) electric steels, produced in acid or basic electric-arc and induction furnaces; by the method of electro-slag melting; or by the methods of electron-beam and plasma-arc melting;

(d) steels produced by combined processes (successive melting in two plants, for instance, in a basic and an acid open hearth in the duplex process; successive melting in three plants, for instance, a Bessemer converter, open-hearth furnace, electric-arc furnace, in the triplex process, etc.).

Classification of steels by their purpose is as follows: common steels, structural steels, tool steels, and steels having special physical and chemical properties.

Structural steels are in turn divided into constructional steels and machine steels. These kinds of steel are used to make various machines, machine tools, metallic structures of bridges, building frames, etc. Carbon steels containing not more than 0.6 per cent C, and also carbon steels with small additions of chrome and nickel, and sometimes of manganese, are widely employed in various branches of economy.

Tool steels are intended for making various cutting tools, such as drills, cutters, etc., elements of forging and stamping presses, gauges, and so on.

Steels having special physical and chemical properties include stainless steels, acid-resisting steels, high-temperature steels, non-magnetic steels, transformer steels, dynamo sheet steels, and other alloy and high-alloy steels.

Ball-bearing steel of high purity (refined from oxides, sulphides and globules) contains around 1 per cent C and 1.5 per cent Cr.

High-quality carbon steels and carbon steels alloyed with some other elements are specially produced for automobile and aviation industries.

Rail steel, tyre steel, spring steel, shipbuilding steel, tube steel, etc. are special kinds of carbon steel alloyed with small amounts of other elements, with more rigorous specifications as regards the content of impurities.

Other kinds of carbon steel are boiler sheet steel, fire-box steel, various kinds of rolled steel (tee-steel, channel steel, sectional steel, etc.)

Quality classification of steels. Plain, quality and high-quality steels are distinguished, the classification being mainly determined by the contents of sulphur and phosphorus. Plain steels are allowed to contain up to 0.05 per cent S and P; in quality steels, the content of these impurities must not exceed 0.04 per cent, and in high-quality steels, 0.025 per cent for each element.

According to their composition, steels are classified as follows:

(a) **Carbon steels.** In steels of this class, variations of their mechanical and other properties are mainly obtained by varying the carbon content in the melt. Thus, there are low-carbon steels, with up to 0.25 per cent C; medium-carbon steels, with 0.25-0.60 per cent C, and high-carbon steels, with 0.61-2.06 per cent C, the manganese content in them being respectively 0.25-0.50, 0.5-0.9, and 0.3-0.9 per cent.

Carbon steels may be made killed, semi-killed or rimming. Rimming steels usually contain not more than 0.23 per cent C, or 0.07-0.10 per cent C in mild grades; semi-killed steels have approximately the same carbon content and around 0.07-0.10 per cent Si; the content of manganese in rimming and semi-killed steels is 0.3-0.4 per cent.

(b) **Alloy steels** are steels which, apart from the additives common for carbon steels, also contain some special alloying elements (such as Cr, Ni, Mo, W, etc.) improving their mechanical and other properties. Three groups of alloy steel are distinguished according to the degree of alloying. The total content of alloying elements in steel (except for carbon) is as follows: below 2.5 per cent in low-alloy steels; 2.5-10.0 per cent in medium-alloy steels; and above 10.0 per cent in high-alloy steels.

Chapter Four

SLAGS OF STEELMAKING PROCESSES

The role of slag in the steelmaking process is extremely important. The chemical reactions between the slag and metal are directed towards attaining an equilibrium, because of which the composition of the metal at the end of a melt is largely decided by the composition of the slag. The temperature and chemical composition of the slag determine its physical properties: viscosity, thermal conductivity, and surface tension. These properties of the slag affect the intensity of erosion of the refractory lining of a converter or open-hearth furnace and dissolution of the lining in the slag, the intensity of heat transfer from the flame to the bath of an open-hearth furnace (which determines the rate of heating of the bath and therefore the productivity of the furnace), the rate of supply of oxygen to the metal and therefore the rate of oxidation of impurities. In the reaction chamber of the open hearth the slag forms a protective cover which to some extent or other (depending on the properties of the slag) prevents absorption of nitrogen, hydrogen and sulphur from the flames by the liquid metal.

THE ROLE OF SLAG DURING MELTING

Let us consider, by way of example, the role of slag during various periods of open-hearth melting. Since the conditions of absorption of oxygen by the bath are different during these periods, the slag must serve as a regulator directing the process in a desired direction (either oxidation or reduction); provide most favourable conditions for refining the steel from harmful impurities; absorb the oxidized impurities rising to the surface of the metallic bath; provide conditions ensuring a minimum loss of iron and other valuable elements from the bath; be sufficiently viscous to permit free evolution of gases from the boiling bath.

Slag is formed from the oxides of the components of the metallic charge, fluxes and ore, the lining of the furnace or converter, the impurities of the metallic charge (soil, sand), etc.

The slag-forming components may be divided into three categories according to their properties (see Table 4).

Table 4

Main Components of Open-hearth Slag

Acid oxides	Basic oxides	Amphoteric oxides
SiO_2	CaO	Al_2O_3
P_2O_5	MgO	Fe_2O_3
TiO_2	FeO	Cr_2O_3
V_2O_5	MnO	V_2O_3
	Na_2O	
	K_2O	

The most decisive influence on slag properties is exerted by SiO_2 and CaO. The content of iron oxides, in particular of FeO, in a free state (not chemically combined) determines the activity, i.e., oxidizing power, of slag.

Alternations in the composition of slag during melting. Since all the silicon and most of the manganese in the charge are oxidized at the beginning of melting, and the lime passes gradually into the slag, the main components of the initial slag are FeO, MnO, and SiO_2. The most important role in the initial slag of a melt is played by silicate compounds of iron and manganese, which have a low melting point. In the basic process, however, even at the first stage of melting the slag absorbs phosphorus oxides, first as iron triphosphate $(FeO)_3P_2O_5$ and then as calcium tetraphosphate $(CaO)_4P_2O_5$.

Lime, the concentration of which in the slag gradually increases, displaces iron and manganese oxides from the silicates, thus forming various calcium silicates:

$$2FeO \cdot SiO_2 + 2CaO = (CaO)_2SiO_2 + 2FeO$$

$$2MnO \cdot SiO_2 + 2CaO = (CaO)_2SiO_2 + 2MnO$$

In the basic process, the content of CaO in the slag increases during the melting, so that the mineral composition of the slag becomes more complicated (Fig. 12).

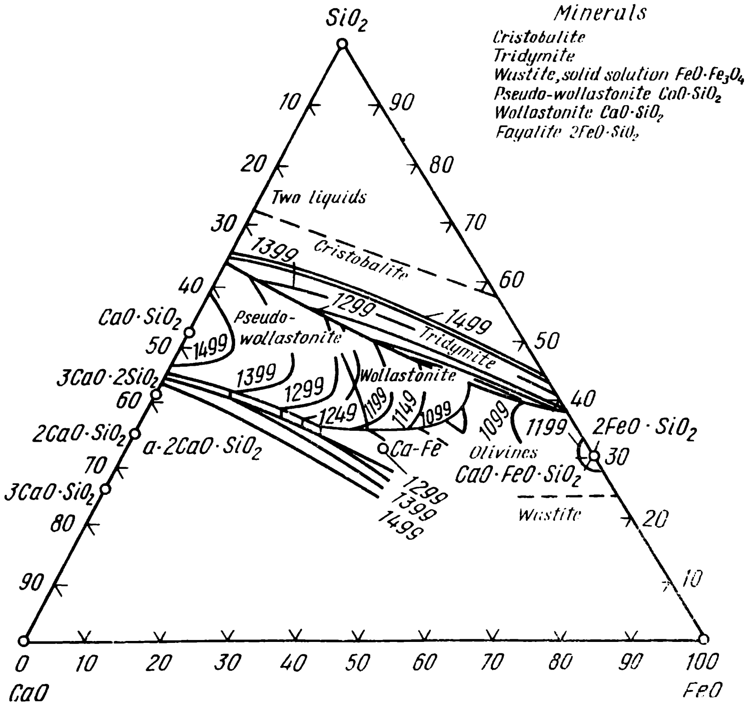


Fig. 12. State diagram of the ternary FeO-CaO-SiO_2 system

Along with the formation of iron and calcium silicates in basic slags, compounds of CaO with iron oxides (calcium ferrite), MnO, MgO, Al_2O_3 and other components capable of forming chemical compounds may also be involved in the system.

Note that the data on the mineral composition of slags come from their analysis in the solid state. In modern views on slags, however, the picture is the one of full or partial dissociation of certain compounds in the molten state.

The method of considering the structure of slags as of molecular solutions of oxides is mainly used for quantitative evaluation of the interaction between the slag and metal, with a number of assumptions on the composition of oxides being made for the purpose. Thus, Schenck considered probable the existence of such compounds in basic slags as Fe_2SiO_4, Mn_2SiO_4, $CaSiO_3$, $Ca_4P_2O_8$, and $Ca_3Fe_3O_7$.

But N. S. Kurnakov asserts on the basis of the phase diagram of the CaO-SiO_2 system (Fig. 13) that Ca_2SiO_4 rather than $CaSiO_3$ is most probable to exist in molten slag, since Ca_2SiO_4 has a sharp maximum on the liquidus line, while $CaSiO_3$ has a flat maximum. As is known, a compound dissociates the stronger, the flatter is its maximum on the liquidus line.

Chipman et al. considered that CaO, MgO and MnO may possess similar properties and that they partially combine into molecules with SiO_2, P_2O_5, Fe_2O_3, and Al_2O_3, the remaining portion being present in the free state. It is conditionally assumed that double molecules $(R_2SiO_4)_2$ and $(RSiO_3)_2$ exist in the slag, with CaF_2 and FeO regarded as neutral components present in the free state.

The process of slag formation may be regarded as that of neutralization of acid oxides by basic ones with the formation of salts.

Thus, the chemical theory of slags makes it possible to give a correct formal description of the reactions between slag-forming components and metal and to perform thermodynamic calculations. It has served as the basis for developing the theory of steelmaking processes and enabled metallurgists to find means for comprehensive control of the melt.

But the chemical theory distorts the physical nature of the processes occurring in the slag melt, so that even the best approximation between calculated values and experimental data cannot serve as evidence to the effect that the structural model of the liquid slag melt is correct. A number of established facts, such as electrolysis of molten slags, data on their electric conductivity versus viscosity, re-

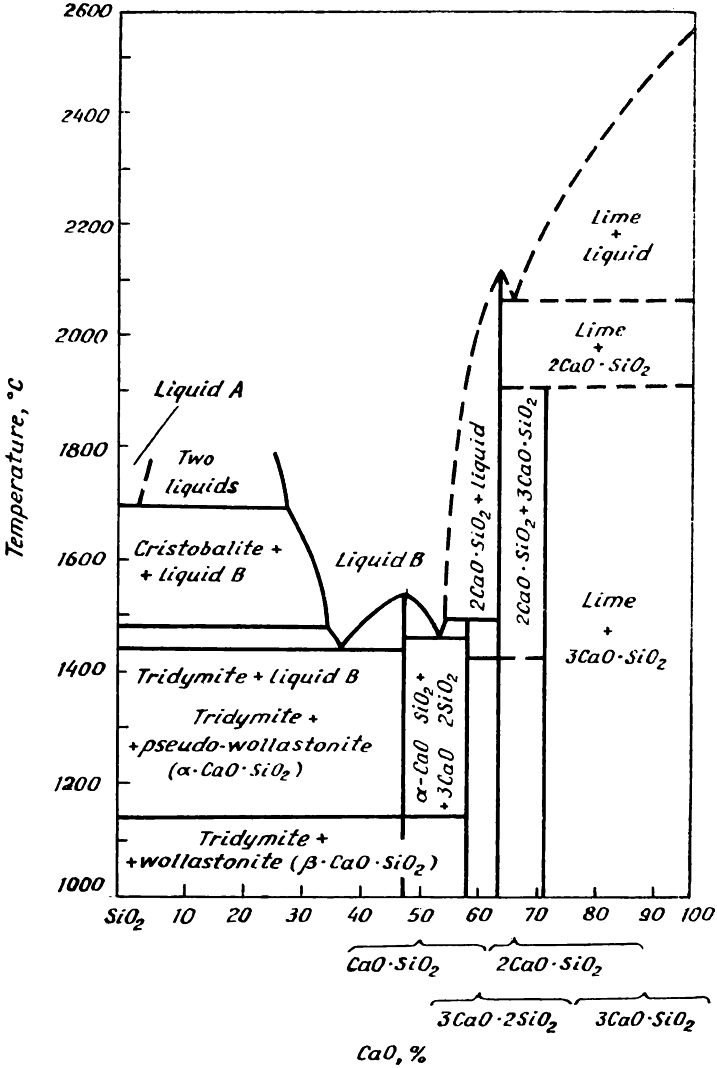


Fig. 13. State diagram of the SiO_2-CaO system

sults of X-ray diffraction analysis of solid slags, have shown that slags are strongly liable to electrolytic dissociation.

According to the ionic theory of slags, oxides, their compounds, and sulphides are present in a dissociated state in the slag: oxides and sulphides dissociate into corresponding cations Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and anions O^{2-}, S^{2-}, and oxide compounds (silicates, phosphates, ferrites, and aluminates), into corresponding cations and complex anions SiO_4^{4-}, PO_4^{3-}, AlO_3^{3-}, etc.

Thus, liquid slag may be considered to be a melt composed of simple cations Fe^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, simple anions O^{2-}, S^{2-}, SiO_4^{4-}, PO_3^{3-}, AlO_4^{3-}, AlO_2^-, FeO_2^-, FeO_4^{2-}, OH^-, F^-, and complex anions $(K_xO_y^-)$ of various complexity. In basic slags the simplest silicon-oxygen groups Si_4^{4-} are formed, in which one atom of silicon is surrounded by four atoms of oxygen (the ratio $O : Si = 4$). In acid slags, which contain much silica, these groups are combined into more complicated silicon-oxygen aggregates of the type $Si_xO_y^{2-}$, for instance, SiO_3^{2-}, $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$, $Si_6O_{18}^{12-}$, in which the $O : Si$ ratio is equal to 3 or 2.5.

A perfect ionic solution should satisfy the following requirements: it should be composed of ions only; the closest neighbour of any ion must always be an oppositely charged particle; likely charged ions are fully equivalent as regards their interaction with neighbouring particles. The activity of each ion in such a solution is equal to its ionic proportion.

In real slags, these conditions cannot be fulfilled, especially the third, since various ions have different sizes, and therefore, the forces of interaction between unlikely charged particles will be different for the same electric charges, these forces increasing with a reduction of particle size.

Cations and anions are charged and therefore tend to approach each other. At the same time, as has been found by electronographic analysis, the actual number of charges of ions is less than that determined by the valency of the atom. For instance, SiO_2 actually contains the ions Si^{2+} and O^-, but not Si^{4+} and O^{2-}; CaO, ions of $Ca^{1.6}$ and $O^{1.6}$ instead of Ca^{2+} and O^{2-}. This is an indication that not only ionic, but also covalent bonds can exist which result in the formation of closed atomic groups.

The energetic non-equality of ions causes a non-uniform distribution of individual ions in the melt: in basic slags, Ca^{2+} ions are disposed preferably near SiO_4^{4-} ions, thus tending to form groups of calcium orthosilicate $2Ca^{2+}(SiO_4)^{4-}$, while Fe^{2+} ions are concentrated at oxygen anions O^{2-}. On the other hand, strong anions O^{2-} and S^{2-}, having a large charge-to-radius ratio, are grouped with strong cations Fe^{2+} and Mn^{2+}, while weak anions SiO_4^{4-} and PO_4^{3-} are grouped with weak cations Ca^{2+}, Mg^{2+}. These unstable groups may be destroyed in some places of a slag melt and appear in others. But it does not mean that neutral molecules of said compounds exist in molten slags.

Thus, real slags, as distinct from perfect ionic solutions, may be regarded to be microheterogeneous and sometimes macroheterogeneous. The oxidizing power of such slags in the baths of steelmaking furnaces is decided by the concentration of iron cations and active concentration of oxygen anions:

$$\Sigma\,(\mathrm{O})_{sl} = N_{(\mathrm{Fe}^{2+2})} \cdot N_{(\mathrm{O}^{2-})} \cdot f_{(\mathrm{O}^{2-})}$$

where $f\,(\mathrm{O}^{2-})$ = coefficient of activity of oxygen, which takes into account the fact that part of oxygen anions are present in more complicated groups, which reduces the oxidation potential of the slag.

The ionic theory of slags is so far unable to consider the interaction of slag and metal on a strictly theoretical basis, without using coefficients experimentally arrived at, since simple and reliable methods do not yet exist to calculate the activity of slag components and equilibrium constants of the processes at various temperatures. On the other hand, the ease of operating with molecular concepts when studying the direction of a metallurgical process, the many years' attachment of engineers to write reactions in molecular form, and finally, the specialist literature and practical recommendations based on the molecular concepts of slag structure, still make it impossible to abandon their use.

CHEMICAL COMPOUNDS IN SOLID SLAGS

The study of the mineral composition of slags discloses the existence of a wide variety of binary, ternary, and more complex chemical compounds in slags. For instance, the following principal compounds may be found in slags:

silicates: $FeO \cdot SiO_2$ (in molten slag); $(FeO)_2 \cdot SiO_2$; $(MnO) \cdot SiO_2$; $(CaO) \cdot SiO_2$; $(MnO)_2 \cdot SiO_2$; $(CaO)_2 \cdot SiO_2$; $(CaO)_3 \cdot SiO_2$; $MgO \cdot SiO_2$; $(MgO)_2 \cdot SiO_2$; $Al_2O_3 \cdot SiO_2$; etc;

phosphates: $(FeO)_3 \cdot P_2O_5$; $(MnO)_3 \cdot P_2O_5$; $(CaO)_3 \cdot P_2O_5$; $(CaO)_4 \cdot P_2O_5$; $(MgO)_3 \cdot P_2O_5$; etc;

aluminates: $FeO \cdot Al_2O_3$; $CaO \cdot Al_2O_3$; $MgO \cdot Al_2O_3$; etc;

ferrites: $FeO \cdot Fe_2O_3$; $CaO \cdot Fe_2O_3$; $(CaO)_3 \cdot Fe_2O_3$; $(CaO) \cdot (Fe_3O_4)$; etc.

The more complex compounds include:

monticellite $CaO \cdot RO \cdot SiO_2$ (where R is Fe, Mn, or Mg);
merwinite $3CaO \cdot RO \cdot 2SiO_2$;
silicocarnotite $5CaO \cdot P_2O_5 \cdot SiO_2$;
nagelschmidtite $7CaO \cdot P_2O_5 \cdot SiO_2$;
thomasite $6CaO \cdot P_2O_5 \cdot SiO_2 \cdot 2FeO \cdot SiO_2$;
stedite $3(3CaO \cdot P_2O_5) \cdot CaO \cdot 2CaO \cdot SiO_2$; etc.

The mineral composition of slags is largely influenced by the chemical composition of the metallic charge, and mainly by its phosphorus content (the last four compounds in the list above come from conversion of high-phosphorus charges), and also by the various fluxes employed in the process, especially fluorspar.

At any given moment, both compounds and their decomposition products exist in slag. The concentration of free oxides determines the main properties of slag, i.e., its oxidizing power, basicity, etc.

BASICITY OF SLAGS

The simplest criterion of basicity is the ratio of the CaO and SiO_2 components in the slag, taken as mass percentages or molar proportions.

For conversion of charges having a high phosphorus content, other formulas (in percentages) should be used:

$$\frac{CaO}{SiO_2 + P_2O_5}; \quad \frac{CaO - 1.18P_2O_5}{SiO_2}; \quad \frac{CaO}{SiO_2 + 0.634P_2O_5}$$

In steelmaking practice, basic slags are termed low-, medium-, and high-basic, according to their basicity value, *viz.* 1.0-1.5, 1.8-2.2, and 2.5-3.2 respectively.

PHYSICAL PROPERTIES OF SLAGS

The density of slag is a function of the densities of its components. The densities (g/cm^3) of the principal slag components at room temperature are as follows:

CaO	3.40	FeO	5.70
MgO	3.65	Fe_2O_3	5.24
SiO_2	2.26	MnO	5.40

The heavy components, FeO, Fe_2O_3, and MnO, have the biggest effect on the density of slag. The dependence of density on the total of the slag components is shown graphically in Fig. 14.

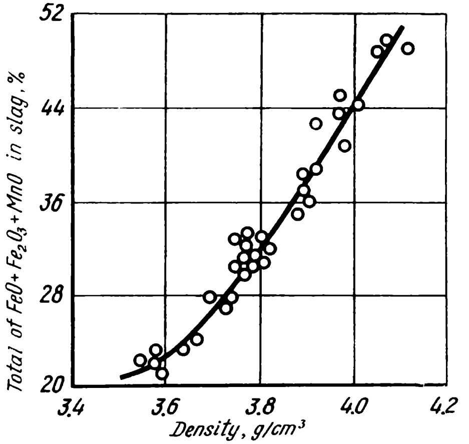


Fig. 14. Density of basic slag as a function of the total of heavy oxides

VISCOSITY AND FLUIDITY OF SLAG

The viscosity η is the most important physical property of molten slag. The activity of slag largely depends on its viscosity, which in turn is a function of its chemical composition and temperature.

The inverse of viscosity is termed fluidity, $\Phi = 1/\eta$. The unit of dynamic viscosity is the poise (P), whose dimension is g/cm·s.

Kinematic viscosity ν is the ratio of the dynamic viscosity η of a substance to its density ρ. It is measured in stokes (cm^2/s).

The viscosity of one poise is the viscosity at which a force of 1 dine must be applied to move a layer of liquid of an area of 1 cm^2 past an adjacent layer of the same liquid being at a distance of 1 cm from the first one with a speed of 1 cm/s.

The dynamic viscosity of water at 25°C is 0.0089 P; of steel at 1595°C, 0.025 P; of slag of medium density at 1595°C, 0.20 P, and of a dense slag at the same temperature, 2 P.

In the mks system, the technical unit of viscosity is 1 kg·s/m^2 = 98.1 P. With an increase of temperature, the viscosity of slags decreases and therefore their fluidity increases (Fig. 15).

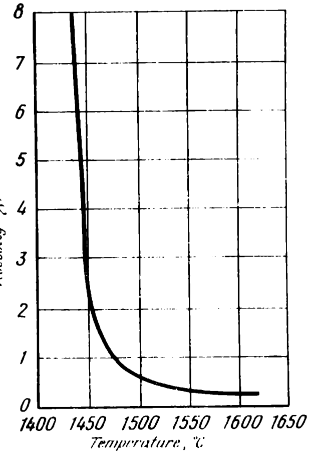


Fig. 15. Dependence of slag viscosity on temperature

CONTROL OF VISCOSITY AND COMPOSITION OF SLAG

The fluidity of slags is usually measured in steel works by means of the Herty viscosimeter (Fig. 16), the criterion of fluidity being how far the 6.4-mm channel of the apparatus is filled with running slag before it solidifies. For acid slags, the apparatus is modified by increasing the diameter of the channel to 9 mm. For the measured results to be comparable, samples must be taken and poured into the apparatus in identical conditions.

The main factor determining the fluidity of slag at constant temperature is its basicity. The higher its basicity, the less fluid the slag becomes.

At present, quite accurate methods exist for controlling the composition of slags by chemical analysis, express

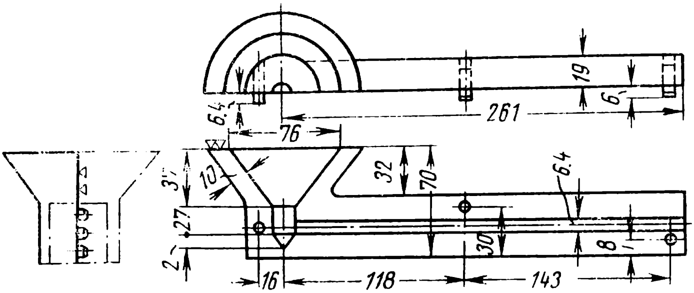


Fig. 16. Herty viscosimeter for measuring slag fluidity

methods for determining the contents of ferrous oxide and silica and basicity of slags, and also methods of spectral analysis.

SLAGS IN THE BASIC PROCESS

The final slag in making plain low-carbon steel contains 6-8 per cent MnO, 10-16 per cent FeO, 1-3 per cent Al_2O_3, 6-9 per cent MgO, 14-18 per cent SiO_2, 38-48 per cent CaO, 1-3 per cent P_2O_5, and 0.1-0.2 per cent S.

It has been found that the total (CaO + MgO + MnO) content in slags is constant at 60 to 65 per cent, which indicates that the basicity of the slag falls with an increase of MnO content on account of decreasing amount of CaO.

Research indicates that the FeO content of slag is dependent on the carbon content of the bath. The rise in basicity during the melt causes the growth in the FeO content of the slag owing to the formation of complex mineral

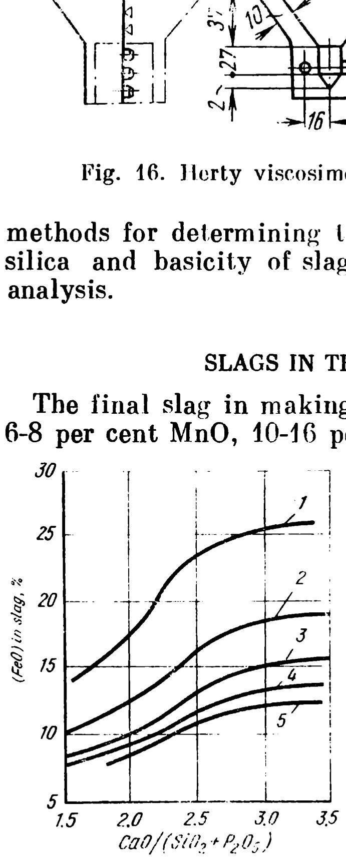


Fig. 17. Dependence of (FeO) content on slag basicity for various concentrations of carbon in metal

1—0.05 per cent; *2*—0.10 per cent; *3*—0.15 per cent; *4*—0.20 per cent; *5*—0.45 per cent compounds (calcium ferrites). It is also observed that FeO content increases more rapidly with lowering of the carbon concentration in the bath (Fig. 17).

The dependence of FeO content in slag on the sum of acid oxides has been found to be as follows:

($SiO_2+P_2O_5$), %	10-12	12-14	14-16	16-18	18-20	20-22	22-24
Fe, % about	20	16	15	14	13	11	9

SLAGS IN THE ACID PROCESS

When the CaO content of slag is low or almost negligible, the total of FeO + MnO + SiO_2 may reach 95 per cent, so that the slag is essentially a ternary FeO-MnO-SiO_2 system with a phase diagram as in Fig. 18.

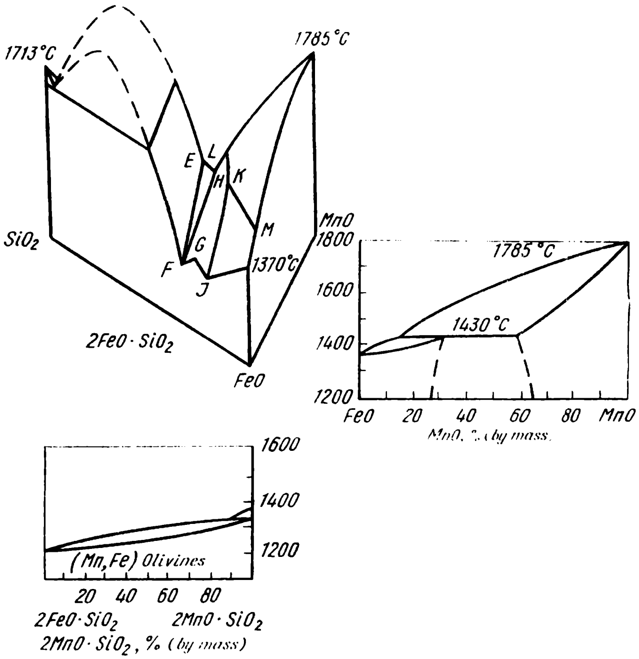


Fig. 18. State diagrams of system constituting acid slags

As will be seen from the diagram, silicate compounds—fayalite $2FeO \cdot SiO_2$, tephroite $2MnO \cdot SiO_2$, and rhodonite $MnO \cdot SiO_2$—are formed in the slag. As regards grünerite $FeO \cdot SiO_2$, its presence in acid slags is now denied. It is not found in the natural state either. According to A. A. Baikov, however, there are not sufficient grounds to disclaim its formation in molten slag. Its transformation into fayalite on cooling may be possible by the reaction

$$2\,(FeO \cdot SiO_2) \rightarrow 2FeO \cdot SiO_2 + SiO_2 + Q$$

The final slag usually contains 50-55 per cent and more of SiO_2. Consequently, it is saturated with this oxide at the melt temperature and is close to equilibrium relative to the compounds constituting the composition of the hearth.

The melting points of the silicates, as will be seen from the diagram, correspond to the minima of the liquidus:

fayalite $2FeO \cdot SiO_2$	1230°C
tephroite $2MnO \cdot SiO_2$	1208°C
grünerite $FeO \cdot SiO_2$	1178°C
rhodonite $MnO \cdot SiO_2$	1270°C

With the addition of CaO to slag (up to 7.8 per cent), calcium silicate is formed as a separate constituent; at higher concentrations of CaO more complex compounds are formed and the content of SiO_2 increases. The following levels of saturation with SiO_2 at 1600°C have been found for FeO-MnO-SiO_2 slag systems on adding CaO:

CaO, %	0	12	18	34
SiO_2, %	48-52	57	60	63

The mineral composition of slags of the SiO_2-FeO-CaO system is shown in Fig. 12. The final slag formed in the active acid process contains 56-58 per cent SiO_2, 4-6 per cent Al_2O_3, 3-4 per cent CaO, 14-16 per cent MnO, and 12-13 per cent FeO. The final slag of the silicon-reducing process contains 55-61 per cent SiO_2, 18-27 per cent MnO, 8-15 per cent FeO, and 4-8 per cent Al_2O_3.

Chapter Five

ACID BESSEMER PROCESS

Up to the middle of the 19th century, methods for producing liquid steel in large amounts were non-existent. At that time, steel was only made by the crucible process, in which wrought iron was smelted together with some carburizing and alloying additives in small refractory crucibles or pots. The process required much time and consumed a large amount of fuel.

In 1855, Henry Bessemer of Great Britain proposed a method of making steel in a very short time (10-15 minutes) by blowing air through liquid iron without expenditure of fuel. The invention was called into being by the necessity of producing large tonnages of metal for casting of artillery guns and construction of railways. The industrial implementation of the process resulted in an undreamed-of growth of steel production, since it became possible to produce much metal at substantially lower expenses than by the puddling or crucible processes.

The process soon became very popular in other countries. Thus, for instance, in Russia the process was mastered already in 1857 at the Vsevolod-Vilvensky works, and in 1859, at the Verkhne-Turinsky and Votkinsky works. The Bessemer process was used there mainly to make commercial iron, but rail steel was also produced with success. The further industrial development of the process in Russia (1872-75) brought about the original Russian version of the Bessemer process for blowing low-silicon pig irons preheated in a cupola or reverberatory furnace. The inventors of this version were D. K. Chernov of the Obukhovsky works in Petersburg and K. P. Polenov of the Nizhne-Saldinsky works.

Before the Great Patriotic War, old Bessemer shops were still in operation at the Petrovsky works, Dzerzhinsky works, Ordzhonikidze works, and Lenin works. In the war years, a Bessemer shop was built in the Urals for conversion of vanadium pig iron by the duplex process. In 1956, Bessemer converters for making semiproduct for open-hearth furnaces were put into operation at the Orsko-Khalilovsky integrated works.

DESIGN OF BESSEMER CONVERTER

The design of the converter is almost the same both for the acid Bessemer and basic Bessemer process. The general view of a bottom-blowing converter is shown in Fig. 19. The body, or shell *1*, which is made from thick steel sheets, bears upon ring *4* provided with two trunnions *5*. In the bottom of the converter vessel is set plug *2* with wind box *3*. Acid Bessemer converters are lined with acid silica brick, and basic converters, with basic dolomite brick. The plug of an acid Bessemer converter has a plurality of tuyere holes to which chamotte tuyeres are attached. In basic Bessemer converters there are no tuyeres but only holes *7* made in the plug during ramming. When the converter is in the

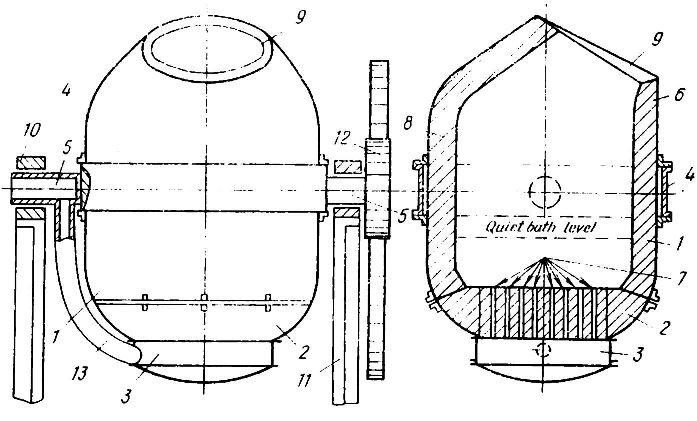
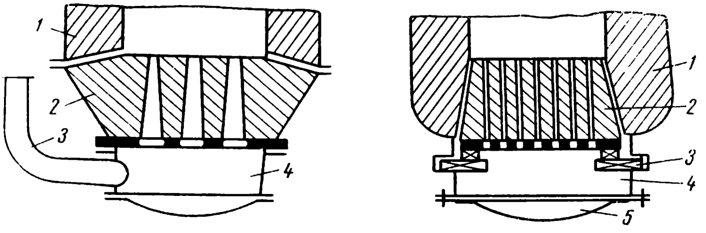


Fig. 19. Diagram of a Bessemer converter

upright working position, air is blown via air duct *13* into the wind box and then through the liquid iron and refines the latter from impurities. During blowing, a pressure of approximately 2 at is maintained in the wind box, so as to counteract the ferrostatic pressure of the iron and prevent the latter against passing into the holes. Since neck *9* is eccentric to the vessel axis, the shell has bend *8* which helps to prevent passage of liquid iron to the holes when the converter is tilted almost to the horizontal position. The neck serves for filling in the converter with liquid iron and pouring out the final steel and slag.



(a) (b)

Fig. 20. Types of Bessemer converter plug

detachable, with tuyeres; *b*—insert-type, with nozzles; *1*—cylindrical portion of vessel; *2*—plug; *3*—pipe connection; *4*—wind box; *5*—wind box bottom; *6*—bars

The trunnions of the converter ring bear on bearings *10* mounted on stands *11*. One of the trunnions is rigidly fastened by a key to gear wheel *12* engaging the rack of the rotating mechanism.

The converter is rotated by a hydraulic mechanism or an electric motor via a reducer gear. The second trunnion is hollow to admit air therethrough in any position of the converter. Small-size converters (up to 15 tons) are lined to a thickness of 350-450 mm. The lining of the converter shell made of silica brick (more than 96 per cent SiO_2) can withstand 1500 melts and more while the rammed plug (a mixture of quartzite powder, chamotte, and fireclay) lasts only 16 to 20 melts. When chamotte tuyeres wear off, they are replaced with new ones, usually after 5 to 6 heats.

A detachable reinforced rammed plug with tuyeres for an acid Bessemer converter is shown in Fig. 20*a*, and an insert plug with holes for a basic Bessemer, in Fig. 20*b*. Each of the tuyeres has 9 to 12 cylindrical holes 12-14 mm in diameter. The number of tuyeres depends on converter size and may be up to 14-30. The calculated cross-sectional area of holes is usually 10-16 cm^2 per ton of iron being blown and the area of the converter side walls, 2.0-2.5 m^2 per ton of iron.

The blast air passes through hot tuyeres or holes and liquid iron and heats up accordingly. It breaks liquid iron into numerous jets and droplets, because of which the volume of the iron increases. This is taken into account in designing and the volume of a converter is increased eight to tenfold to eliminate or reduce splashing out of slag and some metal during the blowing. The depth of the smooth bath in small-size Bessemer converters usually does not exceed 500-800 mm. The unit volume of a converter is 1.2-1.4 m^3 per ton of iron.

The surface of the plug occupied by the holes is called the blast section (blast zone), and the annular surface of the plug between the outer circle of holes and the side walls of the converter shell, the circulation section (circulation zone). The optimum circulation section is considered to be 1800-2000 cm^2 per ton of iron, since it ensures the highest productivity at the maximum amount of blast per unit time.

The pressure of blast air of about 2 at ensures good disintegration of the metal in the blast zone into thin jets and droplets and forms a powerful circulation in the converter space. The result is that a tremendous surface of contact between the metal and air bubbles and slag is formed, so that the rate of oxidation of the carbon in the iron reaches 0.5 per cent per minute. The blow is discontinued only after the converter has been tilted into the horizontal position in order to prevent the passage of metal to the tuyeres. The blast rate is approximately 300-350 m^3 per ton of iron.

MATERIALS FOR THE ACID BESSEMER PROCESS

Pig iron. The pig iron to be used in the acid Bessemer process should contain 0.9-1.25 per cent Si, 0.5-0.8 per cent Mn, not more than 0.07 per cent P, and not more than 0.05 per cent S. Liquid iron is supplied to Bessemer converters from large-size mixers, in which the temperature and composition of the iron are equalized. Sulphur is removed partially during the transport of iron in ladles from blast furnaces to mixers and during the storage in mixers. The greater the manganese content in iron, the larger amount of sulphur can be removed in this way (sometimes up to 30 per cent of its initial content).

An increased content of manganese, on the other hand, may promote splashes of metal and reduce the strength of the lining of the converter shell and plug, which in turn may result in contamination of steel with non-metallic inclusions.

Sulphur and phosphorus brought in with pig iron cannot be removed in an acid Bessemer converter. Moreover, their relative concentrations in the final steel increase somewhat compared with their initial contents in iron owing to oxidation loss of other impurities and partially of iron.

The recommended temperature of liquid iron to be poured into a Bessemer converter is 1290-1320°C.

Iron ore. Acid Bessemer converters are charged with iron ore of the following composition: 85-95 per cent Fe_2O_3; 3-9 per cent SiO_2; 1-3 per cent Al_2O_3; 0.02-0.04 per cent S; and 0.03 per cent P, or with roll scale containing at least 70 per cent Fe and not more than 3 per cent SiO_2.

Mirror iron. Mirror iron is used as dioxidizer in acid Bessemer converters in molten state only, of the following composition: 10-25 per cent Mn; 4-6 per cent C; 2 per cent Si; not more than 0.18-0.22 per cent P; and not more than 0.03 per cent S.

Blast-furnace ferro-manganese. Its composition is 6-7 per cent C; 70-80 per cent Mn; 1.0-1.5 per cent Si, not more than 0.1-0.15 per cent P; and not more than 0.03 per cent S. It is employed either solid or molten, for deoxidation of steel.

Ferro-silicon. 45-per cent or 75-per cent ferro-silicon is used for deoxidation of killed steel.

PERIODS OF THE ACID BESSEMER PROCESS

Upon pouring in liquid iron, the blow is started and at the same time the converter is tilted into the upright working position. The first period (sparking and slag formation) starts just on lifting the converter. The characteristic signs of this period (it lasts roughly for 3-5 minutes) are first a shaft of sparks and then a light-brown flame cone bursting out from the converter neck. During this period, silicon, manganese and part of the iron are oxidized. The oxides of these elements and the oxides of the converter lining form the slag.

During the second period, the carbon of the iron oxidizes intensively. The flame cone gradually grows longer and brighter, then finally becomes dazzling bright and stretches to 5-8 m. Around 90 per cent of the carbon contained in the iron burns to CO, while the remaining 10 per cent of carbon gets oxidized into CO_2, which burns out in the air at the converter neck and thus imparts high brightness to the flame.

In the third period, when there are few impurities left in the melt, the iron again oxidizes intensively. By this time the flame becomes short and reddish-brown, which is indicative of the presence of iron and manganese oxides in the combustion products.

Under certain conditions determined by the temperature and composition of the iron, the first and the third periods may be absent, and therefore the process is finished in a very short time (7-9 minutes). At the end of the process, the converter is tilted to the horizontal, the blow is discontinued, and the final steel tapped through the neck into a teeming ladle. Solid and molten deoxidizers are added into the jet of steel and in the ladle. The whole process lasts 9-10 minutes and the total melting cycle 18-20 minutes. The productivity of modern acid Bessemer converters of a size of 18-35 tons is very high.

The temperature of the iron poured from the mixer into a Bessemer converter is 1250-1320°C. The metal tapped from the converter must be heated up to 1630-1660°C for normal teeming. Therefore, the temperature of iron in the converter must be raised by 320-350°C in a very short period (9-10 minutes).

This is only possible by using liquid iron of a specified composition and carrying out the process within a short time, i.e., without large thermal losses.

The following reactions occur in the Bessemer converter during blowing:

$$Si + O_2 + 3.762N_2 = SiO_2 + 3.762N_2 + 207{,}850 \text{ cal}$$

$$Mn + 0.5O_2 + 1.881N_2 = MnO + 1.881N_2 + 96{,}720 \text{ cal}$$

$$Fe + 0.5O_2 + 1.881N_2 = FeO + 1.881N_2 + 64{,}500 \text{ cal}$$

$$C + O_2 + 3.762N_2 = CO_2 + 3.762N_2 + 94{,}050 \text{ cal}$$

$$C + 0.5O_2 + 1.881N_2 = CO + 1.881N_2 + 26{,}400 \text{ cal}$$

Thermal effects of reactions are usually given in reference books for standard conditions (temperature +25°C and pressure 760 mm Hg). The amount of heat evolved through oxidation of 1 kg of an element at temperatures of the Bessemer process, i.e., within the range of 1200-1600°C, is calculated, in accordance with Kirchhoff's law, by the formula

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Sigma c \, dT$$

where ΔH_T = thermal effect (enthalpy) at a given temperature T

ΔH_{298} = ditto, at $T = 298°K$

$\Sigma c \, dT$ = difference between the enthalpy of the products obtained and that of the starting substances (c being the specific heat)

Additionally, the heat evolved through fluxing by the silica of the slag of the basic oxides FeO and MnO formed in the first period of melt (around 7000 kcal/mol of oxides formed) and also the heats of dissolution of silicon (ΔH = 29,000 kcal/mol) and of carbon ($\Delta H = +8900$ kcal/mol) are taken into consideration.

Table 5 gives the amounts of heat evolved in the bath of an acid Bessemer converter at various temperatures through oxidation of 1 kg of an element, with due regard for the fluxing of FeO and MnO by silica, when the blast consists of common air, oxygen-enriched air (up to 30 per cent O_2), or pure oxygen. It should be kept in mind that in atmospheric air the ratio between oxygen and nitrogen molecules in unit volume is 1 : 3.762, while in the blast enriched to 30 per cent of oxygen it is 1 : 2.33. As a result, when the blast is

Table 5

Thermal Effects of Oxidation of 1 kg of an Element in the Acid Bessemer Process (kcal)

Reaction	Blow	Process temperature, °C		
		1200	1400	1600
$[Si]_{Fe}+\{O_2\}=(SiO_2)$	Air (21 % O_2)	5160	4900	4550
	Oxygen-enriched air (30 % O_2)	5620	5450	5150
	Pure oxygen (100 % O_2)	6350	6310	6200
$[Mn]_{Fe}+0.5\{O_2\}=(MnO)$ with the formation of $MnO \cdot SiO_2$	Air (21 % O_2)	1440	1437	1365
	Oxygen-enriched air (30 % O_2)	1560	1540	1520
	Pure oxygen (100 % O_2)	1790	1780	1740
$[Fe]+0.5\{O_2\}=(FeO)$ with the formation of $FeO \cdot SiO_2$	Air (21 % O_2)	960	750	700
	Oxygen-enriched air (30 % O_2)	1070	890	855
	Pure oxygen (100 % O_2)	1250	1100	1100
$[C]_{Fe}+\{O_2\}=\{CO_2\}$	Air (21 % O_2)	5040	4390	3840
	Oxygen-enriched air (30 % O_2)	6110	5660	5300
	Pure oxygen (100 % O_2)	7820	7690	7620
$[C]_{Fe}+0.5\{O_2\}=\{CO\}$	Air (21 % O_2)	1240	940	660
	Oxygen-enriched air (30 % O_2)	1860	1570	1390
	Pure oxygen (100 % O_2)	2630	2600	2540

changed from atmospheric air to oxygen-enriched air or pure oxygen, the heats of reactions at high temperatures respectively vary. The thermal effects of oxidation of impurities, especially of carbon, sharply increase, mainly owing to the fact that less or no heat is spent to heat up the nitrogen of the air. By considering the thermal effects of carbon oxidation, it may be concluded that, with the oxygen blast,

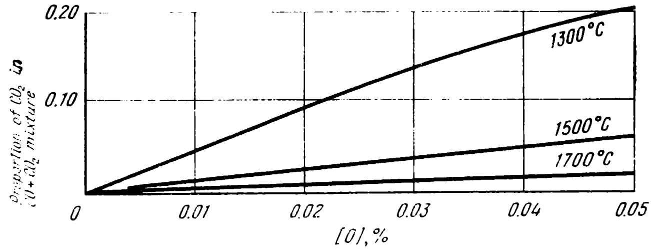


Fig. 21. Composition of CO_2-CO gas mixture in equilibrium with the oxygen dissolved in metal

carbon becomes the main "fuel" in the process, while with the common air blast the main source of chemical heat in the Bessemer converter process is the reaction of silicon oxidation as having the highest thermal effect.

But, though the thermal effect of oxidation of carbon to CO_2 is high, this element cannot be considered the main source of heat in the bath, since the CO_2 that is formed has a low stability under the conditions of the steelmaking process.

As can be seen from Fig. 21, in an equilibrium mixture of gases CO and CO_2 formed through interaction between carbon and oxygen, only a small part of carbon can be present as CO_2. For that reason, the heat contribution of carbon should be evaluated by the reaction C $\rightarrow$ CO, which has a low thermal effect with air blowing. Another reason is that the gaseous products CO and CO_2 are rapidly removed from the converter when still hot, and therefore carry off much heat.

NORMAL, HOT AND COLD CONVERTER RUNS

The role of individual elements of pig iron in increasing the temperature of the converter process may be seen more clearly if we calculate the variations of temperature in the course of oxidation of 1 per cent or 1 kg of an element per 100 kg of pig iron.

Neglecting heat losses to the surroundings and assuming that there are 8 kg of slag (P_{sl}) per 100 kg of pig iron and that the mass of the active layer of the lining 20 mm thick is $P_l = 10$ kg, the rise of temperature can be calculated by the equation

$$\Delta t = \frac{Q}{100c_m + P_{sl}c_{sl} + P_l c_l}$$

where c_m = heat capacity of iron, 0.22 kcal/kg·°C
c_{sl} = heat capacity of slag, 0.32-0.36 kcal/kg·°C
c_l = heat capacity of lining, 0.37-0.43 kcal/kg·°C
100 = mass of iron, kg
Q = thermal effect of oxidation of 1 kg of an element

The calculated data on temperature rise through oxidation of 1 per cent of elements are given in Table 6, which clearly shows that the role of silicon is especially high.

Table 6

Temperature Rise of the Metal in the Bessemer Process Through Oxidation of 1 per cent of Element by Atmospheric Oxygen, °C

Element being oxidized and the product of reaction	Temperature, °C		
	1200	1400	1600
$Si \rightarrow SiO_2$	180	179	170
$Mn \rightarrow MnO$	53	52	51
$Fe \rightarrow FeO$	34	27	26
$C \rightarrow CO_2$	184	160	144
$C \rightarrow CO$	45	34	25

Of large importance is overheating of pig iron. For instance, with pig iron overheated by 100°C, oxidation of

1 per cent silicon additionally gives around 2200 kcal, which is equivalent to an increase of silicon content in the iron by 0.45 per cent.

The productivity of a converter largely depends on how well the heat of the lining is retained between melts. This may be illustrated by the following example. In one case, the process was started when the temperature of the lining was as high as 1500°C; in the other, the lining was chilled down to 900°C by the moment of iron pouring. The difference between the amounts of heat stored in the linings was equivalent to the heat evolved through oxidation of 0.45 per cent silicon. Thus, by the temperature of the pig iron poured into the converter, the content of silicon in pig iron, and the temperature of the converter lining, one can decide whether the melt must be chilled or an additional heat is to be supplied to the process.

45-per cent ferro-silicon may be introduced to heat the metal, which is usually done in the first period of the melt. The richer grade of ferro-silicon is not suitable for the purpose because of its low unit weight and therefore its liability to capture by a thick viscous slag of the acid Bessemer process. If the process is started with the pig iron of normal composition, but poured into the converter at a low temperature, the iron can be heated up by blowing for 2 to 3 minutes with the converter set up into an inclined position (45 degrees to the vertical). Some of the tuyeres in the converter plug will then be free of the metal, and part of the blast air passing over the metal and slag will oxidize an additional amount of iron and also partially afterburn the CO evolved from the bath into CO_2 in the converter. This additional heat is usually sufficient to run the melt normally. After this preliminary blowing, the converter is tilted into the upright position and the blowing is continued in the usual manner. As will be seen from the data of Table 6, it suffices to additionally oxidize 1 per cent of iron in order to raise the temperature of the metal by approximately 30°C. But pouring in of chilled iron reduces the yield of final steel.

Chilling of metal in the converter is usually done by adding steel scrap or iron ore, or by admixing steam to the blast. With chilling by scrap, some heat is spent for its heating and melting, which can be calculated by the formula

$$xQ = (100 + x)\, c_m t_x + (P_1 + P_2)\, c_{s\text{-}l} t_x$$

where x = amount of steel scrap, kg (or percentage when calculated per 100 kg of the metal)
$(100 + x)$ = mass of the metal after addition of steel scrap, kg
c_m = heat capacity of the metal, kcal/kg·°C
c_{s-l} = average heat capacity of the slag and lining, kcal/kg·°C
P_1, P_2 = mass of the slag and lining, respectively, kg
t_x = temperature drop of the metal, °C

One can also calculate how much the temperature of the metal will drop after addition of scrap:

$$t_x = \frac{xQ}{(100 + x)\, c_m + (P_1 + P_2)\, c_{s\text{-}l}}$$

Steel scrap can be introduced either before pouring iron into the converter or during the process, without stopping the blast.

Iron ore and scale are usually added at the beginning of the process, before pouring iron into the converter. These materials are not added during the blowing for they can be carried off by the gases.

Steam dissociates into oxygen and hydrogen in an operating converter, absorbing therewith a large amount of heat. Part of the steam that has not dissociated leaves the converter in hot state and thus chills the melt.

The thermal effects of reactions of oxidation of elements by steam are lower than those for oxidation of these elements by atmospheric oxygen, or are even negative for certain elements. For instance:

$$\mathrm{Si} + \mathrm{H_2O} = \mathrm{SiO_2} + 2\mathrm{H_2} + 91{,}000 \text{ cal}$$

$$\mathrm{Mn} + \mathrm{H_2O} = \mathrm{MnO} + \mathrm{H_2} + 34{,}700 \text{ cal}$$

$$\mathrm{C} + \mathrm{H_2O} = \mathrm{CO} + \mathrm{H_2} - 31{,}400 \text{ cal}$$

while the heats evolved through oxidation of these elements by air are respectively 207,850 cal; 96,720 cal; and 26,400 cal. The method of controlling converter temperature by steam is very convenient in practice. To prevent its condensation steam is usually supplied to the blast box in a superheated state.

When making hard grades of carbon steel, however, care should be taken in using steam, since the hydrogen formed through steam dissociation can partially dissolve in the metal. When choosing the chilling agent, one should keep in mind that iron ore, scale and scrap increase the yield of final steel. In addition, ore and scale increase the oxidizing power of the slag, so that the process can be finished 1-3 minutes earlier. One has also to consider that steam, iron ore and scale, when used as chillers, reduce somewhat the nitrogen content in the final steel.

In the acid Bessemer practice, heating of the melt is resorted to only seldom. The work in the shops is so organized that only short intervals are allowed between tapping of steel from converters and pouring in the next portion of iron. Further, the iron in the mixer is kept at a definite temperature with a silicon content of 0.9-1.3 per cent. Chilling of the melt is done much more frequently, rich iron ore or scale being usually employed for the purpose.

EFFECT OF THE BLAST ON METAL

The motion of liquid metal in the Bessemer converter during the melt cannot be observed directly, because of which the effect of the blast is studied by using a simplified model of the process. Transparent models are used, in which a liquid (mercury, water, glycerine, castor oil, etc.) imitating the metal and slag in the converter are blown with air or other gases; thus the effect of the blast on the metal and slag in the Bessemer converter and the degree of intermixing and mass transfer can be studied. Numerous experiments carried out by a number of researchers suggest the following conclusions:

1. With the air being blown into a liquid through the bottom of the vessel, the air jet first has the shape of a flame cone, and then breaks up into a shaft of bubbles which disintegrate the liquid into droplets. This results in a strong intermixing of the liquid and the formation of air bubbles and slag.

2. During blowing, the liquid begins to rotate and circulates around the periphery of the vessel and between the air jets.

3. As the air pressure is increased, disintegration of the air into bubbles and of the liquid into droplets becomes stronger, i.e., the surface of contact between the air and liquid increases, which in the real process should accelerate the oxidation of impurities in the iron. But the blast pressure can be increased to advantage only to a definite value (2.0-2.5 at). In experiments with mercury at such pressures, the formation of mercury vapours is observed, which can be attributed to a very intimate contact between mercury and air. At higher pressures, disintegration of slag, too, becomes stronger, resulting in a greater amount of slag emulsion formed in the liquid (metal) and therefore in an increased viscosity of the latter. The simulated "metal" thus grows thicker, and prevents a large amount of air to be blown per unit time, since the air breaks into larger bubbles and sputters out more metal, i.e., the conditions of blowing are impaired.

4. Vibrations of the metal surface in the bath are observed during blowing. To have a smoother surface of metal in the converter, the blast should be supplied at such a pressure as to avoid vibrations of large amplitudes. Otherwise, splashes of metal are possible.

5. Once blowing is done with an inclined converter (at 45°), the amount of slag emulsion in the "metal" becomes much smaller than in an upright converter at the same pressure.

OXIDATION OF ELEMENTS IN THE ACID BESSEMER PROCESS

During the blasting of a Bessemer converter, two zones exist where the oxidation of the elements of the iron occurs.

The blast zone is located above the holes of the tuyeres in the bottom. Reactions occur here at the surface of air jets passing out from the holes and at the surfaces of numerous air bubbles detached from the jets, with the oxygen of the blast coming into direct contact with liquid metal and its droplets*:

$$2[Fe] + \{O_2\} = 2(FeO)$$
$$2[Mn] + \{O_2\} = 2(MnO)$$
$$[Si] + \{O_2\} = \{SiO_2\}$$
$$[C] + \{O_2\} = \{CO_2\}$$
$$2[C] + \{O_2\} = 2\{CO\}$$

Owing to rapid oxidation of impurities (Si, Mn, and C) in the surface zones of metal that are in direct contact with oxygen, there takes place diffusion of these impurities and their mass transfer from the bulk of the metal to the reaction surface. But both the diffusion of the elements and the rate of mass transfer lag substantially behind the rates of oxidation of the impurities in the reaction zone, especially in the first period of the process when the iron is still thick and its temperature insufficiently high. For that reason, a predominant portion of the oxygen of the blast reacts with a large number of iron atoms in the liquid iron to form ferrous oxide, while only an insignificant part of the silicon, manganese, and carbon brought to the surface from the bulk of the metal has time to oxidize in that zone.

Thus, if we were to sample metal just from its bulk above the plug holes and determine the content of dissolved oxygen, we could find that the oxygen concentration here is rather high, since the oxygen comes from decomposition of ferrous oxide by the reaction $(FeO) \rightarrow [O] + [Fe]$. Therefore, the blast zone is a zone where oxygen is continuously supplied to the metal.

In the circulation zone, i.e., in the remaining volume of the bath where the metal does not contact directly the oxygen of the blast, there occur the so-called secondary reactions of oxidation of impurities by the oxygen that continuously dissolves in the metal:

$$2[O] + [Si] = (SiO_2); \quad [O] + [Mn] = (MnO)$$
$$[O] + [C] = \{CO\}; \quad 2[O] + [C] = \{CO_2\}$$

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* Reactions of oxidation of silicon and phosphorus are given here conditionally for pure elements. Actually these elements are present in the liquid as groups FeSi and Fe_2P.

Consequently, oxidation of impurities in the acid Bessemer process occurs mainly in the circulation zone, with only an insignificant part of impurities oxidized in the blast zone. Oxidation of silicon and manganese by the oxygen dissolved in the metal results in the formation of a slag phase, since three reactions take place simultaneously:

$$2[O] + [Si] = (SiO_2)$$

$$[O] + [Mn] = (MnO)$$

$$[O] + [Fe] = (FeO)$$

The reaction surface for oxidation of silicon and manganese is very extensive, being composed of the surface of contact of the metal with the silica lining of the converter and with the slag and of the surface of slag inclusions in the bulk of the metal. Therefore, silicon, manganese, and iron, as impurities forming a condensed phase upon oxidation, may directly interact with ferrous oxide at the metal-slag interface where the resistance to removal of reaction products is at a minimum, so that the following reactions take place:

$$[Si] + 2(FeO) = (SiO_2) + 2[Fe]$$

$$[Mn] + (FeO) = (MnO) + [Fe]$$

Acid and basic oxides react between each other and, upon neutralization, form the slag:

$$(FeO) + (SiO_2) = FeO \cdot SiO_2$$

$$2(FeO) + (SiO_2) = (FeO)_2 \cdot SiO_2$$

$$(MnO) + (SiO_2) = MnO \cdot SiO_2$$

A small amount of the lining of the converter is also dissolved by the metal and passes to the slag. The slag of the acid Bessemer process is mainly composed of oxides MnO, FeO, and SiO_2 and soon becomes saturated with silica. The activity of silica in these products is equal to unity, since in the process of blowing the silica comes in contact with the acid lining of the converter, which, too, is composed mainly of silica.

The metal also comes in contact with the silica lining and the silica-saturated slag. For that reason the equilibrium content of dissolved oxygen at a given temperature and a constant activity of silica is determined for the first period of the process by the content of silica, as follows from the equilibrium equation:

$$K_{\mathrm{Si-O}}=\frac{a_{\mathrm{SiO_2}}}{[\%\ \mathrm{Si}][\%\ \mathrm{O}]^2}=\frac{1}{[\%\ \mathrm{Si}][\%\ \mathrm{O}]^2}$$

whence

$$[\%\ \mathrm{O}]=\sqrt{\frac{1}{K_{\mathrm{Si-O}}[\%\ \mathrm{Si}]}}$$

A change in the manganese content at a given concentration of silicon does not alter the activity of silica in the oxidation products. This can be explained by the fact that the SiO_2 concentration in the slag of the acid Bessemer process is always higher than that corresponding to the composition of iron and manganese disilicates. For instance, $MnO \cdot SiO_2$ and $FeO \cdot SiO_2$ contain 45.4 per cent SiO_2, while the SiO_2 content in normal acid Bessemer slags reaches 55-65 per cent. Therefore, the oxidation products are saturated with silica and the activity of silica in them may be compared with that of pure silica, i.e., equated to unity.

As can be seen in Fig. 22, in the first period of the acid Bessemer process, with 1 to 1.5 per cent silicon contained in the metal and at a relatively low temperature (up to 1470°C), it is the silicon that controls the oxidation of the melt even when the carbon content of the metal is as high as 3 to 4 per cent.

Yet, notwithstanding the fact that silicon, unlike manganese, can be in equilibrium with a lower concentration of oxygen, the oxidation of manganese and silicon occurs at the same time. An explanation may be in that proper conditions for rapid removal of the oxidation products from the reaction zone are required for the reaction to proceed intensively. The product of manganese oxidation, MnO, being a basic oxide, is fluxed quickly in the acid slag and therefore the activity of manganese in the slag is low, which ensures further oxidation of manganese in the bath at the expense of a certain retardation of the reaction of silicon oxidation. Thus, silicon and manganese are oxidized simultaneously in the reaction zone, but oxidation of manganese proceeds at a slightly greater rate, since the activity of manganese oxide in the slag is less than that of SiO_2.

It follows from the graphs in Fig. 22 that in the first period of the process, when the melt heated up to 1300°C contains around 4 per cent C and 1.0-1.5 per cent Si, a noticeable oxidation of carbon is impossible, as the high concentration of silicon present in the melt at this temperature results in a lower residual content of oxygen. As is known, for the reaction [O] + [C] → {CO} to proceed, the actual ratio of carbon concentration to oxygen concentration in the metal should exceed the equilibrium value, i.e.,

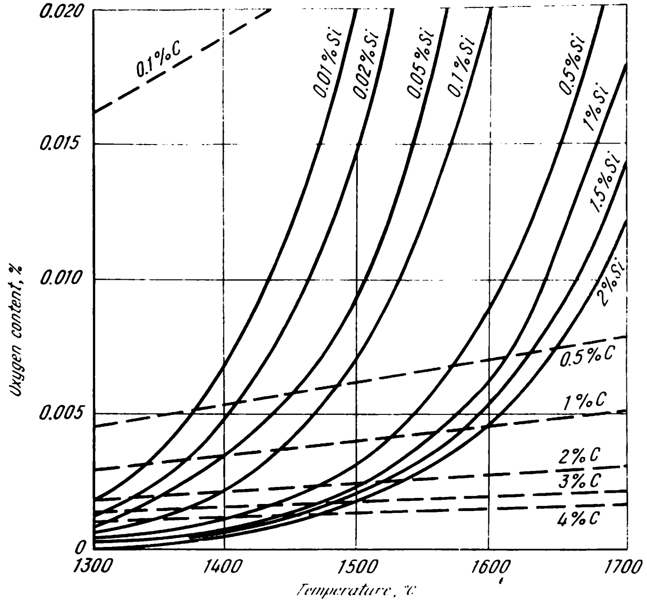

Fig. 22. Equilibrium concentrations of oxygen in iron melt at various concentrations of silicon and carbon ($p_{CO} = 1$ at)

$$[\%\,C]\,[\%\,O] > \frac{p_{CO}}{K_C}$$

Owing to the oxidation of silicon and manganese in the first period the temperature of the melt increases and its viscosity reduces appreciably. At a temperature of 1450-1480°C the second period begins. By this moment only small concentrations of Mn and Si remain in the melt.

When analyzing the possibility of oxidation of carbon (see Fig. 22) in the second period, it is assumed that p_{CO} is 1 at. Actually the pressure of the carbon monoxide evolved in bottom-blown Bessemer converters is not large (around 0.4 at). The formation of CO bubbles and their removal are facilitated in the converter owing to air and nitrogen bubbles always present in the metal. In addition, removal of reaction products is promoted by the air jets.

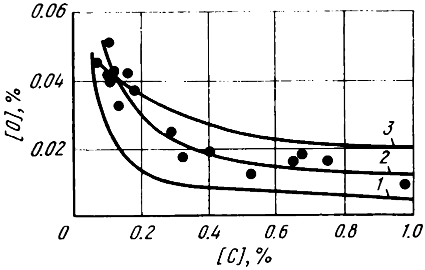

Fig. 23. Dependence of oxygen concentration on carbon content in an acid Bessemer melt

1—equilibrium line during blow at 1600°C; 2—actual oxygen concentration in metal; 3—oxygen in equilibrium with ferrous oxide in the slag at 1600°C

Beginning with the second period and to the very end of the process, carbon acts as the regulator of oxidation of the bath (Fig. 23). With the carbon content of the bath dropping below 0.15 per cent, the concentration of oxygen dissolved in the metal increases; the total number of bubbles in the metal decreases owing to the lower rate of carbon oxidation, and the actual concentration of oxygen increases compared with its concentration corresponding to the equilibrium with carbon monoxide in gas bubbles (Fig. 23).

As will be seen in Fig. 24, during the first and the second period, when silicon and carbon control the concentration of the oxygen dissolved in the bath, the degree of oxidation of the bath is maintained at a relatively low level. But as

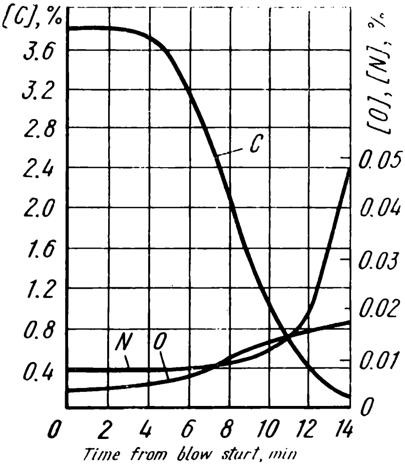

Fig. 24. Variations of contents of carbon, oxygen and nitrogen during an acid Bessemer heat

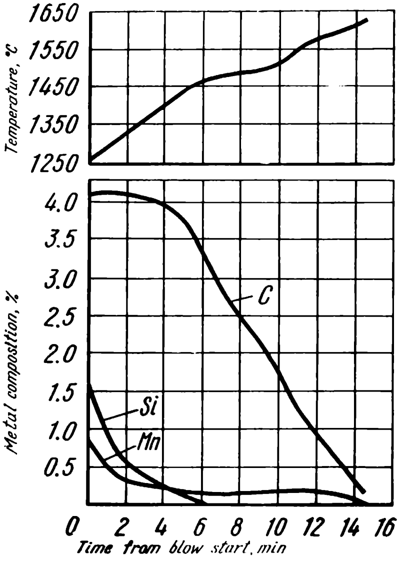

Fig. 25. Oxidation of impurities and variations of metal temperature in the course of an acid Bessemer heat

soon as the carbon content in the bath has decreased substantially, the concentrations of oxygen and nitrogen begin to rise.

The third period is called the period of flame drop. During this period, which starts after the carbon content has reduced to 0.08-0.10 per cent, oxidation of carbon decelerates even more, despite the high concentration of oxygen in the bath. If small amounts of silicon and manganese have been left in the bath, they are oxidized by the blast to some extent, depending on the temperature at which the process is finished. The greater this temperature, the larger amount of silicon (from 0.02 to 0.05 per cent) will be left in the metal.

When the acid Bessemer process is run "with overblowing", to obtain a specified carbon content, the third period may be absent.

The total course of the acid Bessemer process is shown in Fig. 25. As will be seen the temperature of the melt increases in the process by 380°C and the impurities C, Mn, and Si are oxidized completely.

The contents of sulphur and phosphorus in the metal increase somewhat in the process owing to the total oxidation loss of other impurities and iron. Sulphur and phosphorus cannot be removed from the metal in an acid Bessemer converter, since the converter lining is made of acid refractories and fluxes are thus not applicable in the process.

SLAGS OF THE ACID BESSEMER PROCESS

Apart from silicon, manganese and iron oxides, the lining (which is subject to erosion) and partially the blast-furnace or mixer slag that get into pig iron also may contribute to the formation of slag in the converter. When high-silicon pig iron is employed, the lining of the converter is not eroded, but, on the contrary, grows thicker through the formation of skull. This reduces the volume of converter and causes splashes of metal and slag during the melt. Silica skull can be removed by adding sodium chloride into the converter before pouring iron or by running some melts in succession with high-manganese pig iron. The high-manganese slags that are then formed dissolve the skull. A long operation of the converter with the use of high-manganese pig iron can however cause premature wear-off of the lining and, in addition, manganese slags promote splashing.

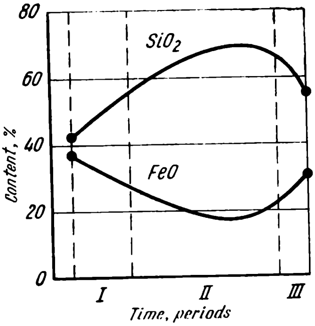

Fig. 26. Variations of FeO and SiO_2 contents in the slag of an acid Bessemer melt

With a normally run converter, the amount of the slag formed is 7-10 per cent of the mass of poured-in iron. Curves of variations of SiO_2 and FeO contents in slag are shown in Fig. 26. As will be seen, the FeO content of the slag is small at the beginning and end of the process. The content of SiO_2 in the slag increases during the melt owing to the oxidation of silicon and dissolution of the lining. Toward the end of the melt the relative content of SiO_2 reduces owing to an appreciable increase of the content of iron oxides in the slag.

The final slag of a normally run process has the following composition: 55-63 per cent SiO_2; 8-12 per cent MnO; 12-18 per cent FeO; 2-3 per cent Al_2O_3; 1-2 per cent Fe_2O_3; and 0.5-1.5 per cent CaO.

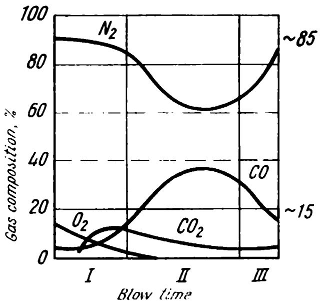

Fig. 27. Variations of gas compositions during the periods of an acid Bessemer heat

VARIATIONS OF GAS COMPOSITION IN THE BESSEMER PROCESS

In the first period of the process, when mainly silicon and manganese are oxidized, the principal components of the gases are nitrogen and partially non-reacted oxygen. With a hot run of the converter, a greater part of the oxygen of the blast air is assimilated and therefore less oxygen can be detected in the converter gases. A good sign of hot running is a high CO : CO_2 ratio in the gases; this means that carbon is oxidized intensively, so that less free oxygen is left in the converter volume to afterburn CO to CO_2. A content of 0.2-0.4 per cent H_2 in the gases may result from decomposition of the moisture of the blast. Variations of the gas composition during the melt are shown in Fig. 27. The content of CO in the gases reaches 35 per cent.

The amount of gases ejected from the converter neck is approximately equal to the amount of blast air, which is 300-350 m^3 per ton of pig iron. The volume of the air blown through the converter during the melt is 10,000 times the volume of the metal in it.

MODIFICATIONS OF THE ACID BESSEMER PROCESS

In the course of its industrial application the Bessemer process underwent certain modifications in various countries, depending on the composition of the pig iron employed and its temperature. With a chemically hot pig iron (i.e., having high silicon and manganese contents) and its high temperature, the first period of the process was absent, and carbon was oxidized at the beginning of the process together with silicon and manganese. When a chemically hot, though insufficiently preheated, pig iron was used, the first period grew longer.

Table 7

Modifications of Acid Bessemer Process Employed in Various Countries

Process modification	Content, %		Temperature of iron preheating, °C
	Si	Mn	
British	2.0-2.5	0.5-0.7	1250-1260
German	2.0-2.5	1.5-2.5	1400-1450
Modern Russian	0.9-1.4	0.6-0.9	1280-1300
Swedish	0.8-1.0	0.1-0.3	1200-1250
American	0.8-1.0	0.5-0.7	1250-1300

Table 7 gives chemical compositions and temperatures of pig irons employed in some modifications of the process.

The type of modification depends on the chemical composition of pig iron and its temperature before pouring it into the converter, since the combination of these factors inevitably results in a more intensive burning of some elements and lower oxidation of others. In its modern version, where still employed, the process uses pig iron with around 1.3 per cent silicon and 0.8 per cent manganese, its temperature before pouring being 1300°C, i.e., the modern Russian version is employed (see Table 7).

DEOXIDATION AND CARBONIZATION OF ACID BESSEMER STEEL

Deoxidation is aimed at combining the excess oxygen dissolved in steel. When making rimming steels, deoxidation is made only by ferro-manganese which is introduced into the ladle in the form of small lumps (less than 100 mm in size) in order to reduce its oxidation loss.

Mirror iron and ferro-manganese are used for deoxidation only in a molten state, by pouring them into the jet of steel being tapped from the converter. When the mass of the deoxidants to be introduced into the ladle is more than 2 per cent of the mass of the charge, only liquid deoxidants are commonly employed.

When making killed steels, ferro-manganese, 45-per cent ferro-silicon, and aluminium are used as deoxidants. Ground ferro-silicon is first given to the jet of steel, and then aluminium. All deoxidants must be introduced before the ladle is filled to half its height.

When calculating the required amount of deoxidants the oxidation losses of their elements are taken as follows: 10 per cent for carbon, 25 per cent for manganese, and 25 per cent for silicon. Before usage, ferro-alloys are melted in a cupola, reverberatory furnace, or electric furnace.

PROPERTIES AND APPLICATIONS OF ACID BESSEMER STEEL

Acid Bessemer steels produced in bottom-blown Bessemer converters differ in their mechanical and technological properties from basic open-hearth steels of comparable composition.

The beneficial properties inherent solely in acid Bessemer steels are as follows: good filling of roll grooves enabling rolling of complex-shape sections with a high accuracy; good weldability in forging and pressing; good machinability; higher ultimate and yield strengths than those of open-hearth steels of the same composition; and better wear resistance to friction and crumpling, especially in rail Bessemer steel.

On the other hand, acid Bessemer steels have some serious drawbacks. They poorly yield to electric welding and thus cracks often appear near weld seems; they are highly brittle, especially at subzero temperatures. The latter defect can be characterized by appreciably lower and varying values of impact strength at various temperatures than for open-hearth steels. Because of their high cold brittleness, rails made of acid Bessemer steel cannot be employed in northern regions of the USSR. Other drawbacks are poor magnetic permeability and electric conductivity.

All drawbacks of acid Bessemer steels can be attributed to increased contents of phosphorus (up to 0.07-0.09 per cent) and especially of nitrogen (up to 0.015-0.025 per cent). As has been shown earlier (see Fig. 24), the content of nitrogen in acid Bessemer steels increases extremely rapidly at temperatures approaching the final temperatures of the process. Afterwards, when the metal is cooled, nitrogen separates from the supersaturated solution in the form of nitrides which cause ageing of steel (increase of its strength and impairment of plastic properties). Because of its poor plasticity, the possibilities of application of acid Bessemer steel are considerably narrowed. It may be used only for manufacture of non-critical articles, such as bolts, nuts, welded tubes. On the other hand, rails made of acid Bessemer steel show a very high durability when used in southern regions.

The production of acid Bessemer steels can be characterized by the following technico-economical indices:

Converter capacity	15-35 t
Blowing period	12-15 min
Tap-to-tap time	20-25 min
Number of melts per day with two converters in operation	90-130

Annual output of the shop:	
with three 20-ton converters	700,000 t
with three 35-ton converters	1,500,000 t
Yield of final steel (per cent of the mass of pig iron)	87-89
Mass of pig iron per ton of final ingots	1.10-1.15 t/t
Blast air consumption	300-350 m³/t

The material and heat balances of an acid Bessemer melt are given in Tables 8 and 9. When considering the tables, special attention should be paid to the fact that the yield of liquid metal is relatively low and that a large amount of heat is carried off from the converter by the gases during the melt.

Table 8

Material Balance of an Acid Bessemer Melt (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kg		Output, kg	
Liquid iron	100.000	Steel	91.39
Air	34.800	Slag	7.000
Converter lining	1.000	Iron beads in slag	1.000
		Gases	36.408
Total:	135.800	Total:	135.800

CONVERSION OF CHROME-NICKEL PIG IRON IN ACID BESSEMER CONVERTER

Blast-furnace melting of iron ores of the Khalilovsky deposit produces pig iron of the following approximate composition: 4.2-4.6 per cent C, 1.4-3.4 per cent Si, 0.6-0.9 per cent Mn, 0.6-0.9 per cent Ni, 2.2-3.6 per cent Cr, 0.35-0.45 per cent P, and 0.04-0.055 per cent S. Conversion of pig iron of high silicon and phosphorus contents with chrome present in it entails great difficulties since the slag formed through oxidation of chrome is very thick and high-melting (up to 2100°C) due to the presence of chromium oxides and partially of chromites of the type $FeO \cdot Cr_2O_3$.

Table 9

Heat Balance of an Acid Bessemer Melt (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kcal (%)		Output, kcal (%)	
Physical heat of:		Enthalpy of:	
pig iron . .	27,300 (50.30)	steel	31,800 (58.20)
blast air . .	474 (0.85)	slag	3 395 (6.20)
		converter gases[1] . .	14,841 (27.30)
Heat from oxidation of:			
carbon . . .	12,540 (23.50)	Heat for moisture decomposition	810 (1.50)
silicon . . .	10,900 (20.10)		
manganese .	1 600 (3.00)		
iron	1 510 (2.80)		
Heat of slag formation . .	243 (0.45)	Radiant and convective heat losses	3 721 (6.80)
Total:	54,567 (100.00)	Total:	54,567 (100.00)

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[1] Of these on heating, kcal (%): CO and CO_2, 4015 (7.4); N_2, 10,650 (19,5); O_2, 31 (0.1); and H_2, 145 (0.3)

At present, a process for conversion of this kind of pig iron is employed in which chrome is lost, but nickel is preserved, and besides a possibility arises for making naturally alloyed chromium steel. For this, the pig iron is blown with air in a bottom-blown acid Bessemer converter of a size of 40 tons to produce high-carbon semiproduct, which is then poured into a basic open-hearth furnace to make the final steel, i.e., a duplex process (acid Bessemer converter and basic open-hearth) is performed. The Bessemer converter is lined with silica brick and partially with fire-clay (chamotte) brick.

The reaction of oxidation of chromium in the Bessemer converter can be written as

$$\frac{1}{2}[Fe]+[Cr]+2[O]=\frac{1}{2}(FeO\cdot Cr_2O_3)$$

The equilibrium constant of this reaction is

$$K=\frac{(a_{\text{FeCr}_2\text{O}_4})^{1/2}}{[\%\ \text{Cr}][\%\ \text{O}]^2}$$

and its temperature relationship

$$K=\frac{53{,}100}{T}-26.12$$

As can be seen, chromium is oxidized rapidly provided that the bath has been deeply oxidized and its temperature is

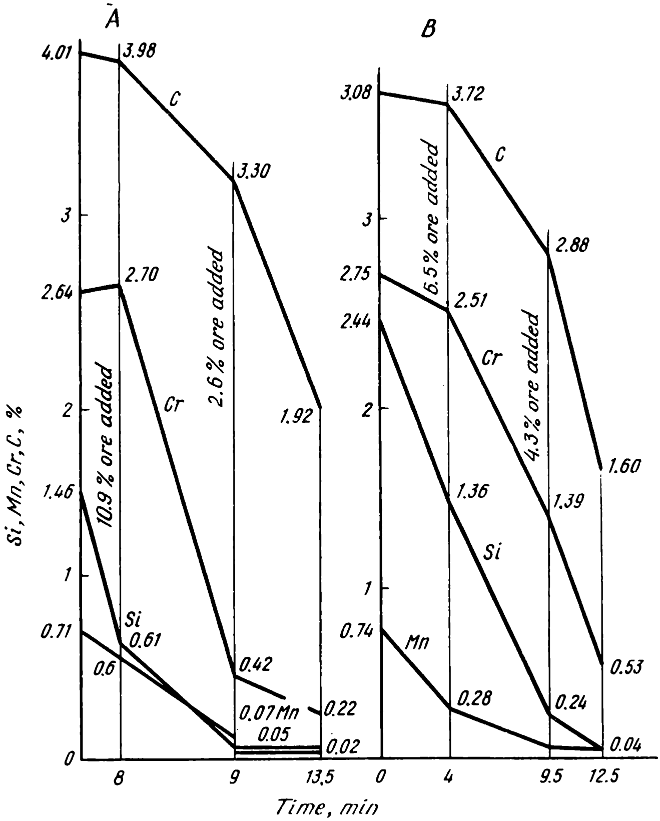

Fig. 28. Oxidation of impurities during blowing Khalilovsky pig iron in an acid Bessemer converter

A—melt I; *B*—melt II

relatively low. But the concentration of oxygen in the metal during the first period of the melt is controlled by silicon, while carbon oxidizes intensively only after the bath is heated to high temperature. Thus, when blowing Khalilovsky pig iron in the converter, the melt should be freed of silicon as fully as possible, since silicon combines much oxygen. Some coolants should be added in order that the bath cannot heat up too quickly.

It is exactly this way that is chosen in practice. Scrap is charged into the Bessemer converter in an amount of 100 kg per ton of pig iron before pouring iron. As the blow begins, almost all the ore specified for the melt is charged into the converter via a chute. This ensures a moderate temperature of the melt (around 1300-1450°C) and an intense oxidation of chromium. After 12 or 13 minutes of blowing, a low-chromium semiproduct is obtained, which is transferred to an open-hearth furnace for making final steel. As has been found, a pig iron containing 0.6-1.5 per cent Si and not more than 1.0 per cent Mn is best suitable for this process; 80 per cent of chromium is oxidized on the average and 43 per cent of carbon.

Figure 28 exemplifies variations in the concentrations of impurities in two melts *A* and *B* of the acid Bessemer process, and Table 10 gives the compositions and temperatures of pig iron and semiproduct and the main components of the slag.

Table 10

Compositions of Khalilovsky Pig Iron, Semiproduct and Slag. Acid Bessemer Process

Melt No.	Content, %					Temperature, °C
	C	Si	Mn	Cr	Ni	
			Pig Iron			
I	4.01	1.46	0.71	2.64	0.72	1190
II	3.80	2.44	0.74	2.75	0.72	1230
			Semiproduct			
I	1.92	0.02	0.05	0.22	0.74	1360
II	1.60	0.04	0.04	0.53	0.78	1460

Continuation

Slag

Melt No.	SiO_2	FeO	MnO	Cr_2O_3
I	32.0	32.0	7.0	23.7
II	44.1	29.4	5.6	12.5

Experiments were carried out at the Voikov iron and steel works on converting Khalilovsky pig iron into semiproduct in a 20-ton basic Bessemer converter. Figure 29 shows variations in the content of impurities in two melts made in this converter. The compositions of pig iron, semiproduct and final slag are given in Table 11. As will be seen from the Table, around 8.7 per cent of iron ore (of the mass of pig

Table 11

Compositions of Khalilovsky Pig Iron, Semiproduct and Slag. Basic Bessemer Process

Melt No.	Content, %					Temperature, °C
	C	Si	Mn	P	Cr	
			Pig Iron			
I	4.39	0.22	1.08	0.60	2.75	1220
II	4.28	0.36	0.95	0.58	2.54	1275
			Semiproduct			
I	1.75	—	0.11	0.60	0.33	1305
II	1.90	—	0.09	0.55	0.69	1330

Slag

Melt No.	SiO_2	FeO	MnO	Cr_2O_3	P_2O_5	CaO
I	12.8	43.6	12.4	31.1	0.24	10.6
II	13.2	19.6	8.5	22.9	0.23	31.1

iron) was charged in the converter during the process. Attempts were made to use lime in the process, but, as was found in the first few melts, this technique was useless,

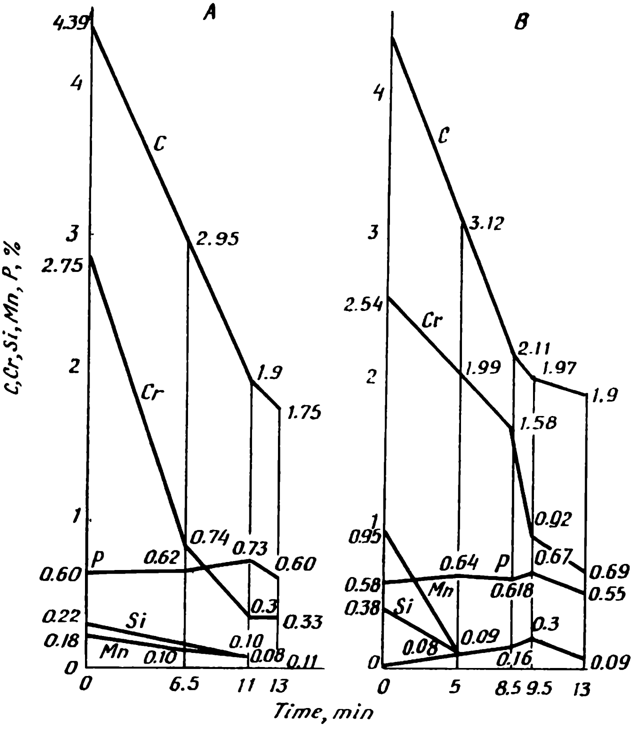

Fig. 29. Oxidation of impurities during blowing of Khalilovsky pig iron in a basic Bessemer converter
A—melt I; *B*—melt II

since dephosphorization of the metal was impossible to achieve because of the high concentration of carbon and, in addition, lime had no time to pass into the slag solution during the short process (13 minutes).

The compositions of the slags in the two processes differed markedly owing to the use of different additives. But in both cases the slags were high-melting, lumpy and low-active relative to the converter lining because of the presence of chromium oxides. The wear of the lining of the basic converter was, however, many times that of the acid one. The yield of semiproduct was 86-95 per cent.

Since the phosphorus content of the semiproduct made in the basic converter was not lower than that of the semiproduct made in the acid converter and the lining of the basic converter was less stable, it may be concluded that basic Bessemer converters are inexpedient for making semiproduct.

As has been found, the content of nitrogen in mild grades of Bessemer converter steel is much greater than in a high-carbon semiproduct. Thus, the contents of nitrogen in semiproducts were (percentages): 0.011, 0.010, 0.020, and in mild steel: 0.022, 0.038, 0.039, 0.040, 0.034, 0.044, 0.045, and 0.047. For that reason it is hardly advisable to perform both chromium removal and dephosphorization in the basic Bessemer converter, since the mild steel produced in it is not suitable as the semiproduct for further conversion in open-hearth furnaces, both as regards its properties and the cost of the whole process.

Another conclusion of importance has been made from the results of conversion of Khalilovsky pig iron in a basic Bessemer converter to produce mild alloy steel. The melt was run with the use of lime, producing steel of the following composition: 0.1-0.2 per cent C; 0.9-1.7 per cent Mn; 0.15-0.35 per cent Si; 0.1-0.2 per cent Cr; 0.03 per cent P; 0.8-1.3 per cent Ni; and 0.04 per cent S. The experiments showed that this method was principally suitable for making steel. The melts were hot, which made it possible to use up to 10 per cent scrap in the charge. The yield of final product was low (80-84 per cent).

Thus, further research is necessary on improving the process of conversion of pig irons of the Khalilovsky type in basic Bessemer converters to achieve better technico-economical indices. The problem will probably be solved in using an oxygen-blown Bessemer converter for making final low-alloy steel, but not semiproduct.

CONVERSION OF VANADIUM PIG IRON

Pig irons smelted from Kerch iron ores contain 0.10-0.14 per cent vanadium, and those made from ores of the Kusinsky and Kachkanarsky deposits in the Urals, up to 0.4-0.6 per cent. In the conversion of these types of pig iron into steel, vanadium oxidizes at an early stage of the melt and passes to slag. The latter serves as the starting material for making ferro-vanadium, the concentration of vanadium determining its value. For that reason, it is highly important to provide the most favourable conditions for vanadium to oxidize as fully as possible and make slag with the highest concentration of vanadium oxides.

Upon reacting with oxygen, vanadium can form several compounds: V_2O_2, V_2O_3, V_2O_4, and V_2O_5. According to the data available, in acid plants vanadium is present predominantly as V_2O_3, and in basic plants, as V_2O_5. It is also known that vanadium trioxide V_2O_3 forms stable vanadium spinel.

In an acid Bessemer converter, upon oxidation of silicon, provided that the process is run cold by adding iron ore or scale, vanadium oxidizes at a high rate, so that 3-4 minutes after the beginning of the blow its concentration in the metal reduces to 0.02-0.03 per cent.

Cold blowing of the melt is beneficial for obtaining slag rich in vanadium oxides. After running off the vanadium slag, the semiproduct obtained is transferred into another steel-making plant, i.e., a duplex process is performed.

At one of the plants in the Urals, pig iron containing 4.2-4.5 per cent C, 0.38-0.49 per cent V, 0.20-0.30 per cent Si, 0.25-0.30 per cent Mn, 0.1-0.5 per cent Cr, 0.06-0.09 per cent P, and 0.15-0.20 per cent Ti was formerly converted by the duplex process (air-blown basic Bessemer converter — basic open hearth). By blowing during 4-6 minutes in a 23-ton Bessemer converter, vanadium was transferred to slag. The semiproduct obtained (0.04 per cent V) was further converted in an open-hearth furnace. The slag from the converter contained 10-16 per cent V_2O_5.

Table 12 gives data on variations in the composition of the metal in two melts for conversion of pig iron of the

Table 12

Variations of Metal Composition in an Air-blown Basic Bessemer Converter in Conversion of Vanadium Pig Iron

Melt No.	Sample No.	Time from start of blow, min/s	Content in metal, %					Temperature, °C
			C	V	Mn	Si	Cr	
I	1	6-25	4.02	0.15	0.15	0.05	0.26	1360
	2	7-55	3.54	0.09	0.04	0.03	0.15	1360
	3	12-24	2.70	0.04	traces	0.02	0.08	1370
II	1	9-48	3.28	0.07	0.04	0.04	0.10	1315
	2	10-48	2.72	0.06	0.02	0.04	0.12	1315
	3	11-48	2.68	0.06	0.02	0.04	0.12	1320

above-mentioned analysis in an air-blown basic Bessemer converter.

After blowing for 4-6 minutes, the metal and slag were poured into a ladle and, after skimming off the slag, the metal in the ladle was brought to an open-hearth furnace. The yield of vanadium slag was 5-6 per cent of the mass of pig iron.

The experience in the extraction of vanadium from Kerch pig iron in a basic Bessemer converter by short blow without lime, skimming off of the vanadium-containing slag, and further basic Bessemer conversion of the semiproduct into steel has shown that the process is practically feasible, but some special techniques required in the process increase its time and noticeably reduce its technico-economical indices.

Experiments were also carried out on production of vanadium slag and semiproduct from Kerch pig iron in an acid Bessemer converter. After a short blow, the concentration of vanadium in the metal reduced from 0.17 to 0.02 per cent, that of silicon, from 0.40 to 0.01 per cent, of manganese, from 1.10 to 0.10 per cent, and of carbon from 2.7 to 2.0 per cent. The content of V_2O_3 in the slag was within the range of 8.50-11.30 per cent. The average composition of the slag was: 31.80 per cent SiO_2, 17.25 per cent FeO, 33.80 per cent MnO, 2.40 per cent P_2O_5, 9.45 per cent V_2O_3 and traces of Al_2O_3, CaO, and MgO.

Chapter Six

BASIC BESSEMER PROCESS

The availability of large deposits of iron ores rich in phosphorus in some European countries promoted the development of a basic-lined Bessemer converter in which pig iron could be refined from phosphorus. The pig iron employed in the basic Bessemer process contains 3.0-3.6 per cent C; 0.3-0.6 per cent Si; 0.8-1.3 per cent Mn; 1.8-2.2 per cent P; and 0.05-0.08 per cent S. It is tapped from a blast furnace at a temperature of 1200-1220°C.

The material for making the lining of such a converter was developed by Sydney Thomas for which he was granted a patent in 1878. He succeeded in burning dolomite "dead", i.e., in melting its grains. Undercalcined dolomite used till then absorbed moisture and carbon dioxide from the atmospheric air and soon crumbled to powder. The binder for dolomite lining was dehydrated tar.

The composition of burnt dolomite is 1.5-3.0 per cent SiO_2; 1.8-2.8 per cent Fe_2O_3; 1.5-2.0 per cent Al_2O_3; 35.0-36.0 per cent MgO; and 55-58 per cent CaO. Its porosity is 10-12 per cent and unit mass, 2.7-2.9 g/cm^3. Upon burning, grinding and classification into fractions from 0.2 to 10 mm, dolomite is mixed with tar (7-9 per cent of the mass of dolomite) preheated to 80°C; the mass is used to form under high pressure bricks or blocks for lining converters. This material is also used for ramming converter plugs by vibration machines. Blocks are first pressed under a pressure of 30-40 at, and then 300-400 at, with the same position of the mould. The converter lining is laid of raw bricks without mortar and is then burned during a short heating of the converter to 1300°C. The tar of the bricks gets carbonized and firmly binds the bricks.

Table 13

Principal Dimensions of Basic Bessemer Converters

Capacity, t	Total height, m	Outside diameter, mm	Thickness of lining, mm		Plug height, mm	Neck diameter, mm
			lower portion	upper portion		
15	5200	3050	450	400	800	800
25	6200	3700	500	450	800	1000
30	7100	4200	600	500	900	1200
50	7750	6000	1000	600	1000	1300

The thickness of the converter lining is usually 600-800 mm, which enables it to withstand 350-400 heats. The plug of the basic converter has no tuyeres. Before ramming the plug, steel needles are inserted into holes in the bottom plate. Upon ramming the plug, the needles are removed, leaving holes for blasting. Sometimes (for operation with

Table 14

Selected Technical Characteristics of Basic Bessemer Converters

Capacity, t		Bath depth, mm		Average blow rate, m³/min	Average blow time, s, per ton iron	Scrap in charge, %	Tap-to-tap time, min	Area of holes, m² *	Area of plug, m²
new vessel	before repair	new vessel	before repair						
15.5	16.5	622	375	470	46	3.0	35	1.47	2.02
20.0	24.0	606	538	520	46	6.5	30-35	1.73	2.07
23.5	25.0	632	475	526	37	7.5	35-40	1.66	2.95
27.0	31.0	785	450	560	34	6.8	27	2.09	3.14
34.0	38.0	802	443	635	31	6.8	25	2.40	3.78

---

* Net cross-sectional area of holes is 13.7-15.7 cm² per ton iron.

steam-oxygen blast), holes are strengthened with copper tubes. Holes are located in concentric circles over the whole surface of the plug. Rammed plugs are burned in box furnaces during 30 hours. A plug can withstand 60-80 melts. Tables 13 and 14 give the principal dimensions and certain technical characteristics of basic Bessemer converters.

In some European countries, where the deposits of phosphorous ores are rich, the basic Bessemer process has rapidly gained in popularity and its share in the total steel production is still high, as can be seen from the following figures of production of basic Bessemer steel in some countries in 1972:

Belgium	France	Luxembourg	FRG	GDR	England	Sweden
21.8	29.8	55.3	6.1	9.8	2.0	0.4

SPECIFIC FEATURES OF THE BASIC BESSEMER PROCESS

The process differs largely from the acid Bessemer process in visual signs, physico-chemical conditions, and technology. Lime in an amount of 12-15 per cent of the mass of iron is charged into the converter prior to pouring pig iron. The basic lining of the converter and the lime in the charge make it possible to run the process with slags of a sufficiently high basicity, which is of importance for dephosphorization to be carried out successfully. Since it is high-phosphorus pig iron that is converted in the process, the basicity of the slag is determined by the ratio of CaO in the slag to the total of acid oxides of silicon and phosphorus in it. It is advisable that the (% CaO) to (% SiO_2 + % P_2O_5) ratio be greater than 3.0.

Lime used to form slag should be low-burnt and contain 90-92 per cent CaO; 0.5-2.0 per cent SiO_2; 0.6-1.2 per cent Al_2O_3; 1.0-1.5 per cent MgO; and not more than 0.05-0.1 per cent S.

The final slags of the basic Bessemer process are rich in phosphorus oxides. They are employed with success in agriculture as fertilizers. The composition of this slag includes 42-56 per cent CaO, 14-23 per cent P_2O_5, 5-10 per cent SiO_2, 7-15 per cent FeO, 2-5 per cent Fe_2O_3, 2-8 per cent MnO, 2-6 per cent MgO, and 1-3 per cent Al_2O_3. The best assimilation of slag by soil and the best solubility are ensured at 7-9 per cent silica in the slag, which is linked with a certain degree of silicizing (the ratio of oxygen in silica to oxygen in all basic oxides in slag). If the slag of a melt is expected to be low in silica, some bank sand is added to the phosphate slag being skimmed off.

Basic Bessemer slag is tested for solubility in a 2-per cent aqueous solution of citric acid ($C_6H_8O_7$). It should be noted that fluorspar must not be used to reduce the thickness of phosphate slags, since it may impair the solubility of slag in soil.

To obtain the slag even with a minimum content of phosphorus oxides (14 per cent P_2O_5), with the total amount of slag in the converter being 25 per cent of the mass of pig iron, 1.5 per cent of the phosphorus in iron must be oxidized.

PERIODS OF THE BASIC BESSEMER PROCESS

Lime and coolants are charged into the vessel prior to pouring in pig iron if it is known in advance that the melt will be run with excess heat evolved. After pouring in pig iron, the converter is turned up to the working position and at the same moment blowing is started at a pressure of 2.0-2.6 at.

The first period (the period of sparks and slag formation) is characterized by a pale short flame with a reddish tint owing to burning of particles of lime. Manganese, silicon, and part of iron are intensively oxidized during this period. The oxides of these elements and also the eroded lining and the lime form the slag.

Characteristic of the second period, which is called the foreblow, is an elongated flame. This period usually begins just after the temperature of the metal has risen to an appropriate value owing to the exothermic reactions that take place in the first period. But this temperature is lower than it is at the same stage in the acid Bessemer process and the flame is less bright, since basic Bessemer pig iron is low in Si and Mn. The second period is usually accompanied by splashing and jump-like development of the reaction of carbon oxidation, which is attributed to the moisture in lime.

The third period, called the after-blow, is indispensable in this process. The major part of phosphorus is oxidized during this period. The visual signs of the period are a short flame at the converter neck. By the beginning of this period all the lime passes into the slag melt. This is what ensures oxidation of phosphorus with the formation of stable compounds $(CaO)_3P_2O_5$ and $(CaO)_3P_2O_5 \cdot CaO$ through decomposition of $(FeO)_3P_2O_5$.

Variations in the metal and slag compositions and also in the temperature of the basic Bessemer process are shown in Fig. 30. As can be clearly seen, an intense oxidation of phosphorus begins only at the end of carbon oxidation, owing to the late conversion of lime to an active form. For that reason metal in the basic Bessemer process is always blown so as to reduce its carbon content down to 0.05 per cent. It will be seen in the same figure that CaO content of the slag must be high (more than 45 per cent) in order to oxidize phosphorus intensively.

If the steel of a higher carbon content must be produced, the final soft metal is carbonized in the ladle by adding coke breeze, graphite or anthracite.

OXIDATION OF ELEMENTS IN BASIC BESSEMER CONVERTER

Given below are the reactions of oxidation of impurities in the blast zone, with due regard to the fluxing of the acid oxides being formed by lime:

$$\begin{gathered}
Si + O_2 + 3.762N_2 + 2CaO \\
= (CaO)_2 \cdot SiO_2 + 3.762N_2 + 239{,}400 \text{ cal}
\end{gathered}$$

$$Mn + 0.5O_2 + 1.881N_2 = MnO + 1.881N_2 + 192{,}500 \text{ cal}$$

$$Fe + 0.5O_2 + 1.881N_2 = FeO + 1.881N_2 + 64{,}500 \text{ cal}$$

$$C + O_2 + 3.762N_2 = CO_2 + 3.762N_2 + 94{,}050 \text{ cal}$$

$$C + 0.5O_2 + 1.881N_2 = CO + 1.881N_2 + 26{,}400 \text{ cal}$$

$$\begin{gathered}
P + 2.5O_2 + 2.5 \times 3.762N_2 + 4CaO \\
= (CaO)_3P_2O_5 \cdot CaO + 2.5 \times 3.762N_2 + 525{,}000 \text{ cal}
\end{gathered}$$

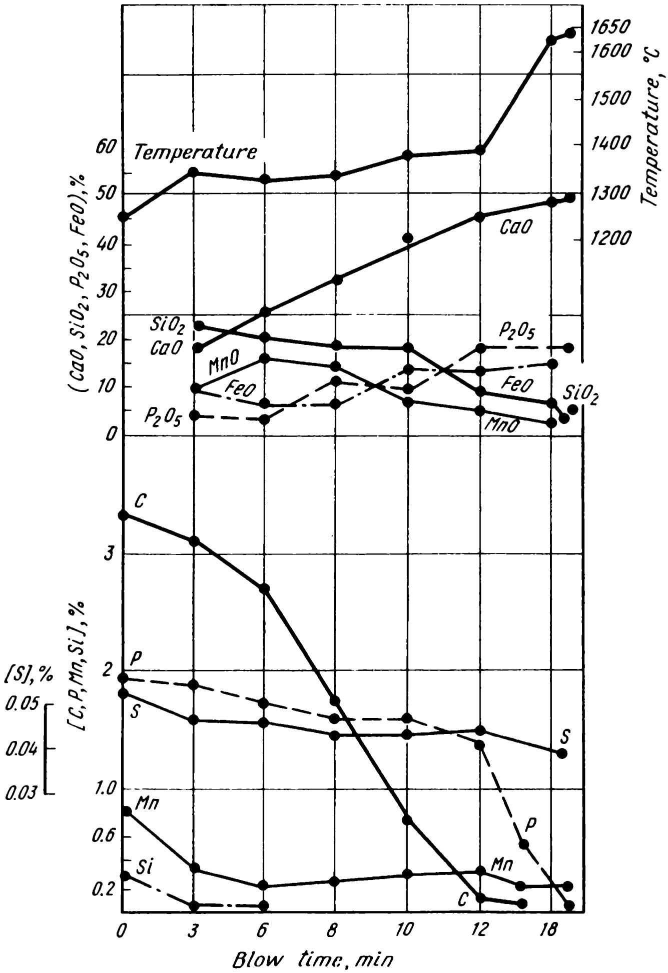

Fig. 30. Variations of metal and slag composition and temperature during a basic Bessemer heat

The thermal effects of oxidation of impurities in a converter are somewhat lower than those given above, since they reduce with increasing temperature. Table 15 gives the amounts of heat picked up by the bath at various temperatures from oxidation of 1 kg of elements in a basic Bessemer converter including fluxing of acid oxides by lime, with the blast consisting of atmospheric air, oxygen-enriched air (30 per cent O_2), or pure technical oxygen (conditionally 100 per cent O_2).

It may be seen from comparing the thermal effects of oxidation of silicon in the acid and basic Bessemer processes that less heat is liberated in the latter case when lime is involved in the reaction, because lime absorbs some heat. Ferrous oxide and manganese peroxide are basic oxides and therefore cannot be fluxed. The total heat from the oxidation of iron and manganese is less in the basic Bessemer process than in the acid process, since the pig iron used contains less iron and manganese silicates, owing to which the heat of slag formation is lower.

The role of individual elements of pig iron in the basic Bessemer process can be seen more clearly if we consider the rise of temperature through oxidation of 1 per cent of an element or 1 kg of an element per 100 kg of pig iron, taking account of fluxing of acid oxides by lime:

Temperature, °C	1200	1400	1600
Element being oxidized and products of reaction:			
$P \rightarrow (CaO)_3P_2O_5 \cdot CaO$	127	106	85
$Si \rightarrow (CaO)_2 \cdot SiO_2$	150	132	115
$Mn \rightarrow (MnO)$	38	37	35
$Fe \rightarrow (FeO)$	24	18	16
$C \rightarrow \{CO_2\}$	148	123	107
$C \rightarrow \{CO\}$	36	26	18

As can be seen, the main source of heat is phosphorus. Though during its oxidation silicon liberates much heat and thus raises the temperature of the process, the basic Bessemer pig iron is low in silicon and its content must not be increased, since silicon oxides erode the lining in the first and second periods of the process, when lime has not as yet completely dissolved in the slag. In addition, an increase

Table 15

Thermal Effects of Oxidation of 1 kg of an Element in the Basic Bessemer Process, (kcal)

Reaction	Blow	Process temperature, °C		
		1200	1400	1600
$2[P]_{Fe}+2.5\{O_2\}+$ $+4(CaO)=$ $=(CaO)_3P_2O_5\cdot CaO$	Air (21% O_2)	4350	3760	3040
	Oxygen-enriched air (30% O_2)	4860	4350	3750
	Pure oxygen (100% O_2)	5700	5350	4900
$[Si]_{Fe}+\{O_2\}+$ $+2(CaO)=$ $=(CaO)_2\cdot SiO_2$	Air (21% O_2)	5160	4780	4150
	Oxygen-enriched air (30% O_2)	5600	5300	4770
	Pure oxygen (100% O_2)	6350	6090	5790
$[Mn]_{Fe}+0.5\{O_2\}=$ $=(MnO)$	Air (21% O_2)	1313	1310	1240
	Oxygen-enriched air (30% O_2)	1450	1440	1400
	Pure oxygen (100% O_2)	1670	1660	1650
$[Fe]+0.5\{O_2\}=(FeO)$	Air (21% O_2)	830	625	570
	Oxygen-enriched air (30% O_2)	940	760	725
	Pure oxygen (100% O_2)	1120	980	970
$[C]_{Fe}+\{O_2\}=\{CO_2\}$	Air (21% O_2)	5040	4390	3840
	Oxygen-enriched air (30% O_2)	6110	5660	5300
	Pure oxygen (100% O_2)	7820	7690	7620
$[C]_{Fe}+0.5\{O_2\}=$ $=\{CO\}$	Air (21% O_2)	1240	940	660
	Oxygen-enriched air (30% O_2)	1860	1570	1390
	Pure oxygen (100% O_2)	2630	2600	2540

in the silicon content of the iron may reduce the solubility of phosphate slags. High-manganese iron is also undesirable, as it may retard the oxidation of phosphorus.

Since hydrodynamic conditions in a bottom-blown basic Bessemer converter and an acid converter are alike, the predominant oxidation of iron impurities in the circulation zone should be expected here too. The only difference is that because of a colder start of the basic converter process, a somewhat greater proportion of carbon (up to 17 per cent) will be oxidized to CO_2 in the basic converter than in the acid converter (9-12 per cent C).

The processes of oxidation of impurities and fluxing of oxides can be described by the following reactions:

$$2[O] + [Si] + 2(CaO) = (CaO)_2SiO_2$$

$$[O] + [Mn] = (MnO)$$

$$[O] + [C] = \{CO\}$$

$$2[O] + [C] = \{CO_2\}$$

$$5[O] + 2[P] + 4(CaO) = (CaO)_4P_2O_5$$

or

$$2(FeO) + [Si] + 2(CaO) = (CaO)_2SiO_2 + 2[Fe]$$

$$(FeO) + [Mn] = (MnO) + [Fe]$$

$$5(FeO) + 2[P] = (P_2O_5) + 5[Fe]$$

$$(P_2O_5) + 3(FeO) = (FeO)_3P_2O_5$$

$$(FeO)_3P_2O_5 + 4(CaO) = (CaO)_4P_2O_5 + 3\,(FeO)$$

As in the acid Bessemer process, silicon controls the content of oxygen dissolved in the bath in the first period of the basic Bessemer process, as the reaction front for oxidation of manganese and silicon at the surface of the lining and the slag and at the surface of particles of slag inclusions is quite large, and therefore oxygen in the metal cannot noticeably exceed the value that conforms to its equilibrium with silicon. Phosphorus cannot oxidize in the first period, since the lime has not yet fully dissolved in the slag.

For the reaction given above, the equilibrium concentration of oxygen and silicon is determined by the equation

$$\log K_{Si} = \log \frac{1}{[\%\ Si][\%\ O]^2} = \frac{31,000}{T} - 12.15$$

and that of oxygen and phosphorus, by the equation

$$\log K_P = \log \frac{a_{Ca_4P_2O_5}}{[\%\ P]^2[\%\ O]^5 a_{CaO}} = \frac{71,667}{T} - 28.73$$

As silicon and manganese are being oxidized, the concentration of oxygen dissolved in the bath increases and, when the temperature of the metal becomes sufficiently high and its viscosity reduces, intense oxidation of carbon begins in the blast zone and circulation zone. From that moment on, carbon controls the oxidation in the bath, but the concentration of oxygen remains above the equilibrium value, since the reaction front for carbon oxidation is relatively small, being confined to bubbles of carbon monoxide and nitrogen.

By the moment when the carbon has been oxidized down to 0.04-0.05 per cent (lower values are hardly attainable because of the carbon present in the tar of the lining), all the lime dissolves in the slag and rather intense oxidation of phosphorus begins, for the bath now has enough oxygen and lime for this reaction to take place. Varying concentrations of the oxygen dissolved in the bath are now determined, as follows from the formula above, by the phosphorus content and the activities of calcium phosphate and calcium oxide in the slag.

The content of manganese first decreases, then rises, and finally decreases again, i.e., has a characteristic peak (see Fig. 30). Manganese is reduced from slag to metal by its reaction with phosphorus:

$$2[P] + 5(MnO) = (P_2O_5) + 5[Mn]$$

during the intense oxidation of the latter. When, however, the metal becomes low in phosphorus, manganese is again oxidized by the oxygen of the blast and passes to slag.

REMOVAL OF SULPHUR FROM BASIC BESSEMER CONVERTER

Since the basic Bessemer process is run in a basic-lined vessel, with lime employed to form slag, one might expect a rather good refinement of metal from sulphur. But actually desulphurization in the basic Bessemer converter proceeds very weakly, since the slag still contains much FeO when lime becomes active to flux sulphur.

Sulphur is easily soluble in metal, because FeS and iron are mutually soluble. The object to be attained here is to combine sulphur into CaS and MnS. Manganese sulphide is formed in iron ladles during transportation of pig iron from blast furnaces and in the mixer, if the content of manganese in the metal is sufficiently high. FeS and MnS in the slag interact with lime by the reactions

$$(FeS) + (CaO) \rightleftarrows (CaS) + (FeO)$$

$$(MnS) + (CaO) \rightleftarrows (CaS) + (MnO)$$

As follows from the reactions, the slag must be low in FeO in order to combine sulphur into a stable compound, which is clearly revealed when the FeO content in the slag is below 5.0 per cent. A high-basic free-running slag is required for successful removal of sulphur. The slags formed in a basic Bessemer converter by the end of the melt are high-basic, but have a low fluidity. For that reason the coefficient of distribution of sulphur between slag and metal is $\eta_S = (S) : [S] \leqslant 4$ to 5. It depends predominantly on the ratio between basic and acid oxides in the slag. With a basicity $B = \%\ CaO : (\%\ SiO_2 + \%\ P_2O_5) > 3.5$, the final slag has a sufficiently high capacity to pick up sulphur.

In the practical basic Bessemer process, cooling of the metal is often resorted to. For this, iron ore, scale or ore-lime briquettes are added to the metal just before the beginning of the third period. If the process is to be chilled with scrap, this is charged into the vessel prior to pouring in pig iron.

CONVERSION OF HIGH-SILICON LOW-PHOSPHORUS PIG IRON

When the pig iron for basic Bessemer conversion is high in silicon, special measures are taken to reduce its silicon content.

In modern practice, preliminary oxidation of silicon is effected by blowing the metal ladles on their way from the blast-furnace shop to the steelmaking shop. Oxygen at a pressure of 3-8 at is blown into the metal via pipes or water-cooled tuyeres, its flow rate being 3-8 m^3 per ton of metal. The temperature of the metal thus rises by 50-80°C. This method can reduce the silicon content of the metal by 50 per cent. Blowing is accompanied by intense fuming because of simultaneuos oxidation of iron. Fumes may be reduced by blowing steam-oxygen mixture (63 per cent steam and 37 per cent oxygen) instead of pure oxygen. In some cases certain oxidants, fluxes, and fluorspar are introduced into the ladle during blowing in order to reduce fuming and intensify the removal of sulphur and silicon.

With a low-phosphorus pig iron used in the basic Bessemer process, the heat balance of the operation is normalized by adding ferro-phosphorus to the melt. If the lining is well heated, it is advisable to carry out the process as follows: to charge only a part of the specified mass of lime into the vessel; perform the first period of melting; skim off the initial slag, charge the remaining lime into the vessel and thus carry through the melting. The amount of the secondary slag formed in the converter is comparatively small, but it is rich in phosphorus oxides to be suitable for further utilization.

The amount of lime to be added to the melt can be rapidly calculated by the empirical formula

$$\mathrm{CaO}(\%) = [\mathrm{Si}\ (\%)\ \text{in iron} + \mathrm{P}(\%)\ \text{in iron}] \times 6$$

DEOXIDATION AND CARBONIZATION OF BASIC BESSEMER STEEL

During deoxidation of basic Bessemer steel, and especially during its carbonization, an unwanted reversion of phosphorus from slag to metal is possible by the reactions

$$(CaO)_4P_2O_5 + 5Mn = 5MnO + 4CaO + 2P$$

$$(CaO)_4P_2O_5 + 5C = 5CO + 4CaO + 2P$$

which proceeds more intensely as the metal temperature rises and the bulk of slag grows too. For that reason mesures should be taken to prevent contact between deoxidants and slag.

Rimming steel is deoxidized with lump ferro-manganese (80-100 mm in size) added to the steel jet at tapping. Following this, aluminium is poured in an amount of 100-300 grams per ton of metal, depending on the residual content of carbon in the melt. Part of this aluminium is sometimes introduced into moulds during teeming so as to control normal boiling of the metal. During deoxidation of killed low-carbon steel, ferro-manganese, 45-per cent ferro-silicon, and aluminium are fed in succession into the jet of metal.

Killed steel of a high carbon content is deoxidized in the same way, but use is made here of molten ferro-manganese or mirror iron poured into the jet of metal tapped from the vessel, and of a carburizer (coke, graphite, anthracite or char-coal in paper bags) added at the same time. After that ferro-silicon and aluminium are introduced.

Semi-killed steel is deoxidized in the following way: ferro-manganese is added to the jet of metal, after which 45-per cent ferro-silicon is introduced to obtain finally 0.07-0.10 per cent Si in the metal. The degree of deoxidation of steel is corrected by aluminium added into the moulds or the central runner (in uphill teeming).

In any case all additions must be made before the ladle is filled with metal to half its height.

As has been shown earlier, blowing in a basic Bessemer converter is finished when metal contains 0.04-0.05 per cent C and 0.04-0.05 per cent P. With such a low carbon content in the melt, the concentration of oxygen may be as high as 0.07-0.09 per cent. Besides, the melt may contain 0.018-0.024 per cent nitrogen. Nitrogen and phosphorus increase the ultimate strength and yield strength of steel, but sharply reduce its plastic properties, i.e., relative elongation and impact strength, especially at subzero temperatures. The combined effect of nitrogen, oxygen and phosphorus impairs the quality of steel. During deoxidation of such a highly oxidized steel, numerous oxide inclusions that are formed cannot be removed completely and remain in the final steel. During solidification of steel, nitrogen separates from the supersaturated solution in the form of nitrides which cause ageing of steel. Because of its susceptibility to ageing, brittleness and poor plastic properties, basic Bessemer steel finds only a limited application.

The principal technico-economical indices in basic Bessemer steel manufacture are as follows:

Converter capacity	18-65	tons
Blow time, minutes:		
air blow	16-20	
oxygen-enriched air blow	12-15	
Yield of final steel, % of mass of iron	85-88	
Amount of slag, % of mass of iron	22-28	
Lime, % of mass of iron	12-18	
P_2O_5 in slag, %	16-22	
Life of lining	300-450	melts
Life of plugs	40-80	melts
Net cross-sectional area of plug holes	15-18	cm^2/t
Blow rate, m^3/t iron	350-450	
Iron used per ton of final ingots	1.15-1.18	t
Annual output of shop:		
with four 25-ton converters	300 000	t
with four 40-ton converters	700 000	t

Tables 16 and 17 give the material and heat balances of a basic Bessemer melt. It should be noted that the yield of final metal is relatively low, and also that much heat is lost in the process with converter gases.

WAYS FOR IMPROVING THE BASIC BESSEMER PROCESS

Research is being carried out in Belgium, France and the Federal Republic of Germany on developing new methods of the basic Bessemer process aimed at reducing nitrogen and phosphorus contents of the final steel. By adding

Table 16

Material Balance of a Basic Bessemer Melt (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kg		Output, kg	
Liquid iron	100.00	Steel	89.615
Blast air	39.763	Slag	20.937
Lime	9.372	Iron beads in slag	1.000
Converter lining wear	1.600	Gases	39.183
Total:	150.735	Total:	150.735

Table 17

Heat Balance of a Basic Bessemer Melt (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kcal (%)		Output, kcal (%)	
Physical heat of:		Enthalpy of:	
pig iron	24,660 (39.3)	steel	32,100 (51.3)
blast air	527 (0.8)	slag	11,700 (18.6)
Heat from oxidation of:		converter gases[1]	14,692 (23.4)
carbon	11,615 (18.5)	Heat for decomposition of:	
manganese	1 600 (2.8)	$CaCO_3$	361 (0.6)
silicon	3 711 (5.9)	moisture	900 (1.4)
iron	3 200 (5.1)	Radiant and convective heat losses	2 902 (4.7)
phosphorus	11,650 (18.6)		
Heat of slag formation	5 692 (9.0)		
Total:	62,655 (100.0)	Total:	62,655 (100.0)

---

[1] Of these for heating, kcal (%): CO and CO_2, 3350 (5.3); N_2, 11,150 (17.8); H_2, 153 (0.2); and O_2, 39 (0.1).

limestone, iron ore and mill scale, each in an amount of 30-65 kg per ton iron during the third period of the process, without stopping the blow, the content of nitrogen can be reduced to 0.008 per cent and that of phosphorus, to 0.045 per cent. These additions promote degassing and reduce metal temperature, both effects being favourable in reducing the solubility of nitrogen in metal.

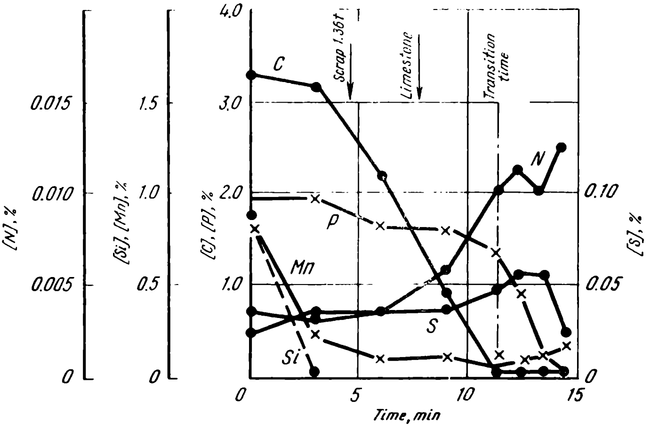

Fig. 31. Variations of metal composition and nitrogen content in a melt with the use of coolants

Figure 31 shows the variations in the contents of impurities in the basic Bessemer metal with the use of coolants (scrap and limestone) added at the moment when the process passes to phosphorus oxidation, and also the variations in the content of the nitrogen dissolved in the metal. As will be seen, the content of nitrogen has decreased somewhat through the action of the coolants. Another example (Fig. 32) shows that addition of iron ore as the coolant to increase degassing, even with oxygen blow, is the best way for shortening the melt time as well as for reducing the nitrogen content in steel, since phosphorus is oxidized at the same time with carbon.

Further search for methods of improving steel quality has helped to find that the nitrogen content of final steel can be lowered by:

(a) finishing the melt at a lower temperature;

(b) reducing the time of contact between blast air and metal;

(c) reducing the depth of the bath;

(d) reducing nitrogen content of the blast air;

(e) shortening the second period of the melt in which the rate of carbon oxidation is very high, while nitrogen concentration in the metal reduces only insignificantly.

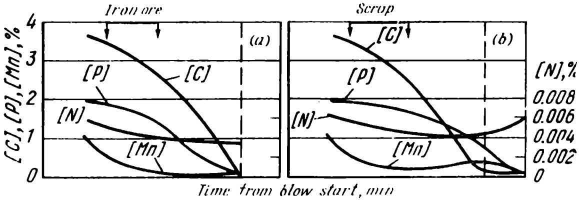

Fig. 32. Top-blowing of metal with oxygen in a 3-ton converter
a— addition of iron ore; *b*—addition of scrap

In order to verify the established relationships, melts have been made with cooling by means of iron ore and mill scale; with the blow of mixtures ($O_2 + H_2O$) and ($O_2 + CO_2$), in which the partial pressure of nitrogen is substantially lower than in the air blast; with the use of lime together with soda; and with the use of steam-air or steam-oxygen-air mixtures.

A process with double blowing has been tested (for making PN steel), in which 50-60 per cent of the specified amount of pig iron and all the lime are first charged in the vessel. The first blow is made to produce mild metal, after which the blow is discontinued and the remaining pig iron is poured in. Vigorous reactions are immediately observed between iron oxides in the slag and impurities of the metal. The second blow is done during 1-2 minutes. The phosphorus content thus falls down to 0.04-0.045 per cent and the content of iron oxides in the slag reduces somewhat. The final steel has a lower nitrogen content than in the common process, since in the first period of the melt the bath is shallower and the duration of contact between metal and blast is shorter. In addition, the total time of the melt is 4 minutes less than in the common process (Fig. 33).

The time of contact between metal and blast air can also be reduced and thus the concentration of nitrogen in final steel lowered down to 0.0070-0.0083 per cent if a common basic Bessemer converter is arranged for side blowing. But this method has not found wide application because of strong splashing and reduced productivity and durability of the converter. Figure 34 shows three possible methods of side blowing of a 30-ton basic Bessemer converter: (a) by keeping the converter in inclined position and specially arranging plug holes; (b) by tilting the converter and thus controlling the depth of the bath; and (c) by using a side-blown turbo-converter (the Chinese People's Republic).

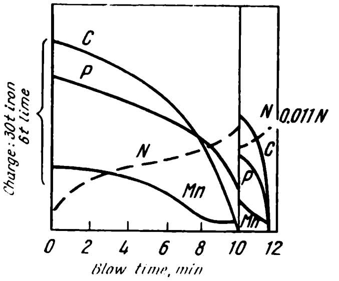

Fig. 33. Variations of metal composition and nitrogen content in the basic Bessemer heat with overblow (PN steel)

Reduction in the phosphorus content of metal is effected through the use of two slags. As the phosphorus content of the metal has dropped down to 0.05-0.08 per cent, the vessel is turned down, the initial high-phosphorus slag is skimmed off, and a new slag is adjusted by adding lime, soda, mill scale and broken fireclay bricks, after which the second blow is done for 15-45 minutes. This method enables the phosphorus content to be reduced to 0.015-0.030 per cent and that of sulphur, to 0.02 per cent. Excessive loss of heat is sometimes compensated for by adding soda and silico-calcium in equal amounts.

D.K. Chernov indicated back in 1876 that oxygen-enriched air might be beneficial for Bessemer converter processes.

With oxygen-enriched air blast, which gives better steel owing to a lower nitrogen content, another beneficial feature is that less nitrogen is supplied with the blast to the metal

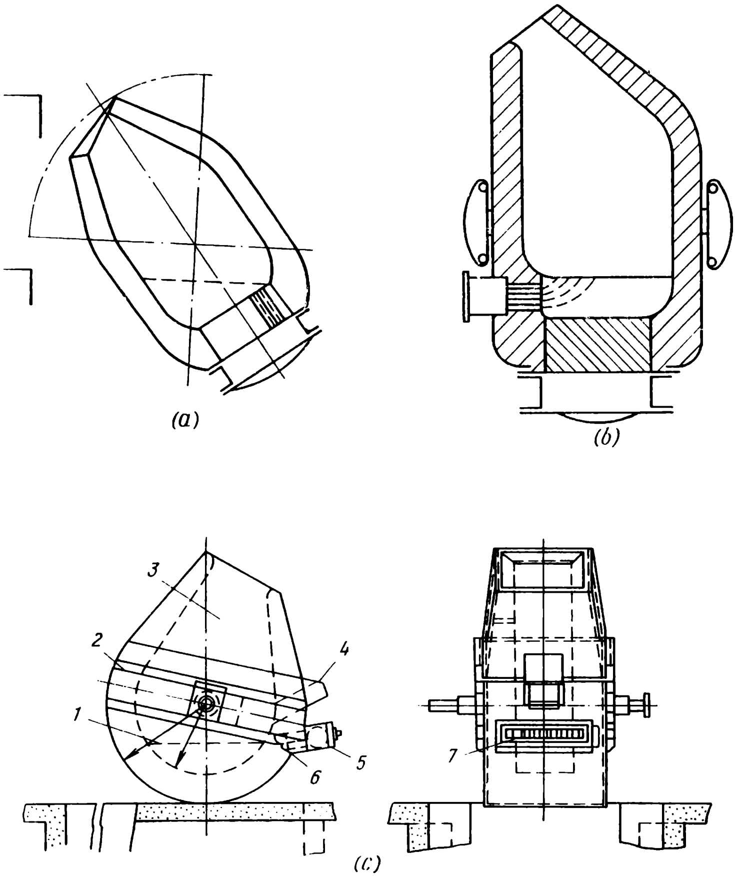

Fig. 34. Versions of basic Bessemer process aimed at reducing nitrogen content in steel

bottom blowing with off-centre nozzles; b—side blowing in a common converter; c—side blowing in a turbo-converter (Chinese People's Republic); 1 bath level; 2—lining; 3—opening for gas sampling; 4—door; 5—wind box; 6—tuyeres; 7—viewhole and therefore less heat is spent to heat up nitrogen. This results in a surplus heat evolved during melting, which makes it possible to increase the solid proportion (scrap, ore or mill scale) of the charge. Limestone is often used as a coolant in this process, because the CO_2 evolved through decomposition of limestone can serve both as an additional oxidant and for bubbling. These additions reduce the content of nitrogen in the gaseous phase, decreasing thereby the absorption of nitrogen by the metal. Further, additions of iron oxides favour earlier dissolution of lime in the slag, which speeds up the reactions of phosphorus oxidation.

Some works employ the following mode of blowing: pig iron is first blown with air during 3-4 minutes, after which the supply of technical oxygen is switched on so as to maintain 30-40 per cent O_2 in the blow mixture. The supply of oxygen is discontinued after the phosphorus content of the metal has dropped down to 0.05-0.10 per cent. Splashing is eliminated by temporarily stopping the oxygen supply. The melt is run with one or two slags in the course of which half of the specified amount of lime is as a rule replaced with limestone.

Table 18 gives comparative data on converter productivity and the contents of nitrogen, phosphorus and sulphur in steel with the vessel blown by air, oxygen-enriched air (three versions), and steam-oxygen mixture.

Research into the behaviour of impurities in bottom-blown melts has shown that metal begins to absorb nitrogen intensively only when the melt becomes relatively low in carbon; before then, the content of nitrogen may even decrease, since carrying-off of nitrogen by bubbles of carbon monoxide occurs with greater intensity than dissolution of nitrogen in the metal. For that reason it is most advantageous to start oxygen-enriched blowing just in the second half of the process when the metal is capable of absorbing more nitrogen. Besides, it is advisable to add limestone and iron ore to the vessel just at this time or a bit earlier.

Figure 35 shows the variations in the concentration of impurities in a basic Bessemer converter blown by oxygen-enriched air, with limestone and iron ore being added to the melt. As can be clearly seen, nitrogen content of the

Table 18

Comparative Data on Basic Bessemer Melts with Various Compositions of the Blow

Parameters	Blow				
	air	oxygen-enriched air (30 % O_2)			steam-oxygen mixture
		I	II	III	
Consumption of materials, % of poured-in iron:					
lime	13-15	13-15	13-15	11-13	13-15
scrap	3-9	15-20	5.5-7.5	—	6-9
limestone . .	—	—	—	3.5	—
iron ore . . .	—	—	2-3	3-4	—
Oxygen consumption, m^3/t iron	—	21	21	21	50
Content in steel, %, of:					
nitrogen . . .	0.0110	0.0082	0.0063	0.0049	0.0023
phosphorus in melts:					
with one slag	0.046	0.046	0.034	—	—
with two slags . . .	—	—	—	0.019	0.019
sulphur . . .	0.034	0.034	0.023	0.024	0.020
Productivity of 16-t converter, t/min	1.1	1.5	1.5	1.5	1.9

melt drops from 0.007 per cent to 0.005 per cent after two minutes of blowing.

The comparison between carbon and phosphorus oxidation in the common air-blown basic converter process and in the process run with oxygen-enriched air blast and with additions of limestone and iron ore is presented in Fig. 36.

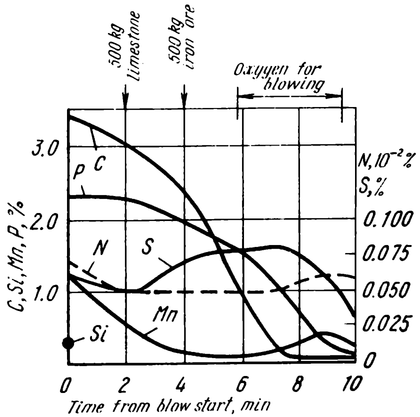

Fig. 35. Variations of metal composition and nitrogen content in a 16-ton basic Bessemer converter during blowing with oxygen-enriched air (30% O_2) with additions of lime and iron ore

As will be seen from the graphs, beginning with the second minute of blasting, when oxidation of silicon has finished, phosphorus burns out quickly and the rate of its oxidation increases even more starting with the oxygen supply to the blast. From that moment on the rate of carbon oxidation becomes almost equal to that of phosphorus.

In this version of the basic Bessemer process, however, the specified limit of phosphorus concentration of 0.04-0.05 per cent is achieved only at a very low final concentration of carbon. Therefore, with this degree of enrichment of air with oxygen (30-40 per cent) it is impossible to form an active dephosphorizing slag at an earlier stage of the melt.

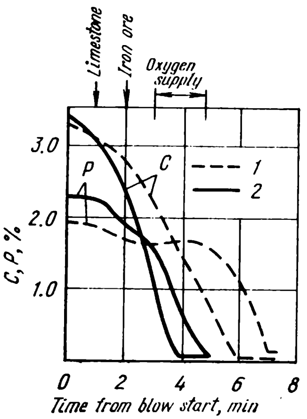

Fig. 36. Intensities of oxidation of C and P in basic Bessemer melts with additions of lime and iron ore (dotted lines: air blow; solid lines: oxygen-enriched air blow)

For that reason, this process is inapplicable for operation "with overblow", i.e., with stopping the blow at a higher concentration of carbon. The metal is blown until the carbon content drops down to 0.04-0.05 per cent and is additionally carbonized in the ladle, when needed, by adding anthracite, broken welding electrodes, etc. For all that the merits of this process are obvious — improved quality of steel with only 0.005-0.007 per cent N and increased productivity of the converter.

With the air enriched to 30-40 per cent O_2, the consumption of oxygen is 20-30 m^3 per ton iron. The life of the converter lining, plugs and holes is the same as with air blow. Plugs stand longer because of the shorter period of blow. The amount of scrap for metal cooling depends on the amount of iron ore introduced in the melt.

CONVERTER BLOWING WITH GAS MIXTURES ($H_2O + O_2$), ($CO_2 + O_2$), *and* ($H_2O + O_2 +$ *air*)

The use of these low-nitrogen gas mixtures is aimed at (a) reducing nitrogen content in final steel; (b) reducing bath temperature in the reaction zone owing to the reaction of dissociation of steam and carbon dioxide (the temperature is also lowered through heating of the portion of H_2O and CO_2 leaving the bath non-dissociated); and (c) speeding up the process through the use of the blow of a higher oxidizing potential than that of air.

Nitrogen content of the metal can be reduced considerably by using any of these mixtures. Thus, for instance, ($H_2O + O_2$) and ($CO_2 + O_2$) mixtures employed for blowing the metal (with tonnage oxygen containing 99.5 per cent O_2) have a very low concentration of nitrogen.

When making low-carbon steels, partial hydrogenizing of the metal can be prevented by using a ($H_2O + O_2$) or ($H_2O + O_2 +$ air) mixture. For steels of higher carbon contents, a ($CO_2 + O_2$) mixture may be used.

When the ($H_2O + O_2$) or ($CO_2 + O_2$) gas mixture is used, the reaction of iron oxidation in the blast zone evolves less heat than in the case of oxidation of iron with oxygen as some heat is spent for dissociation of CO_2 and H_2O:

$$Fe_l + 0.5\{O_2\} = FeO_l; \qquad \Delta H^\circ = -56{,}830 \text{ cal/mol}$$
$$\{H_2O\} = \{H_2\} + 0.5\{O_2\}, \qquad \Delta H^\circ = +60{,}180 \text{ cal/mol}$$
$$\{CO_2\} = \{CO\} + 0.5\{O_2\}; \qquad \Delta H^\circ = +66{,}560 \text{ cal/mol}$$
$$Fe_l + \{H_2O\} = FeO_l + \{H_2\}; \qquad \Delta H^\circ = +3\,350 \text{ cal/mol}$$
$$Fe_l + \{CO_2\} = FeO_l + \{CO\}; \qquad \Delta H^\circ = +9\,730 \text{ cal/mol}$$

i.e., oxidation of 1 kg of iron with oxygen gives 56,830 : 56 = = 1015 kcal, while oxidation with steam absorbs 3350 : 56 = = 60 kcal and that with carbon dioxide, 9730 : 56 = = 174 kcal, with the result that the converter temperature will be lower. As has been found, for a steam-oxygen mixture (supplied at a temperature of 200 °C into the melt, with the degree of steam dissociation reaching 70 per cent) to form the same temperature conditions in the hole zone as the air blow does, it should be composed of 49 volume per cent of O_2 and 51 volume per cent of steam, or respectively 63 and 37 mass per cent.

A similar calculation for the (CO_2 + O_2) mixture, with a 50-per cent degree of dissociation of carbon in the melt, shows that it should consist of 49 volume per cent oxygen and 51 volume per cent carbon dioxide, or 41 per cent and 59 per cent by mass.

The degree of dissociation of steam given above is evidently very near the actual value, since this proportion has been found to be optimal by experience.

BOTTOM BLOWING OF CONVERTER WITH STEAM-OXYGEN MIXTURE

Steam-oxygen blow is most often used when converting high-phosphorus pig irons in basic Bessemer converters. The design and lining of the converter may be left unchanged, but the bottom is reinforced with copper tubes of a wall thickness of 1 mm to protect dolomite refractories against hydration. For the same purpose, the temperature of steam-oxygen mixture in the wind box should be not lower than 200 °C. Therefore, steam must be superheated to 370-400 °C and oxygen preheated in heat exchangers or recuperators before mixing it with steam.

As indicated earlier, it is assumed that steam has no time to dissociate more than to 70 per cent. But if a mixture is composed of 37 per cent steam and 63 per cent oxygen (95% pure), a unit volume of the bath obtains 0.79 m^3 oxygen against 0.21 m^3 oxygen in the air-blow operation. Therefore, it is possible to reduce the total cross-sectional area of holes in the bottom plug. Indeed, in a 25-ton basic converter blown with air the number of holes was 280, while with the application of steam-oxygen mixture their number was reduced to 130 with the same hole diameter. With steam-oxygen blow, the amount of oxygen picked up by the metal from a unit volume of the gas supplied increases sharply and the process is speeded up. It has been established in practice that this kind of blow shortens the melt time by 40 per cent compared with air-blown melt, all other things being the same (see Table 18).

But the principal merit of steam-oxygen blow is a low nitrogen content of the final steel (provided that the tonnage oxygen of a purity not less than 95 per cent is used in the mixture). None of the existing industrial methods of steelmaking is capable of producing steel with such a low nitrogen content as obtained through the use of steam-oxygen mixture (Table 19).

Table 19

Nitrogen Content of Steels Made by Various Processes

Process	Number of melts	Average nitrogen content, %
Basic Bessemer process with:		
air blow	125	0.0100
oxygen-enriched air blow, scrap added	83	0.0083
ditto, iron ore added	43	0.0060
ditto, iron ore and limestone added	20	0.0041
steam-oxygen blow	39	0.0019
Open-hearth process	50	0.0060

During the process, when reactions of dissociation of steam develop most intensively, the hydrogen content of the metal increases sometimes up to 9-14 cm^3 per 100 g of metal.

This circumstance restricts wide application of steam-oxygen blow for making medium-carbon steels because of the probable formation of flakes. The process is recommended only for making mild steels, in which hydrogen content does not rise, since the content of the oxygen dissolved in the metal is large by the end of the melt and therefore hydrogen cannot pass into the solution.

Figure 37 shows the variations in the content of impurities in a steam-oxygen blown melt. As will be seen, the process cannot be finished without overblowing. Even at low carbon concentrations (0.04-0.05 per cent) much phosphorus is left in the metal, which means that the slag has no time to attain its full phosphorus-absorbing power. For that reason, the first phosphorous slag is usually skimmed off at a phosphorous concentration of 0.04-0.06 per cent and soda is added (100 kg per 16 t of metal), after which the vessel is reblown during 10-30 seconds. The steel thus obtained contains 0.0020 per cent N, 0.019 per cent P, and 0.021 per cent S on the average.

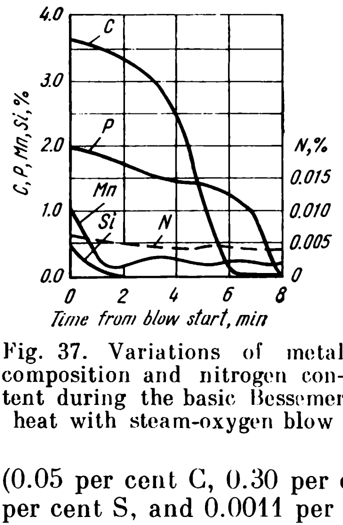

Fig. 37. Variations of metal composition and nitrogen content during the basic Bessemer heat with steam-oxygen blow

At one of the British works, mild steel for deep stamping (0.05 per cent C, 0.30 per cent Mn, 0.020 per cent P, 0.022 per cent S, and 0.0011 per cent N) was produced from high-phosphorus pig iron by blowing 60-ton basic Bessemer converters with steam-oxygen mixture. With the mixture blown from the very beginning, only 10 per cent of scrap could be used in the metallic charge. The consumption of oxygen was 56.6 m^3 per ton of steel, and the purity of oxygen, 99.5 per cent. The process included slagging-off at the moment when 0.04-0.07 per cent P was left in the metal. The amount of slag skimmed off was up to 70 per cent, which contained, apart from other components, 18-21 per cent P_2O_5 and 10-14 per cent Fe. The overblow after slagging-off lasted 30-60 s. The final metal contained only 0.015 per cent of carbon, but this was increased up to 0.05 per cent upon addition of ferro-manganese. The final slag was rich in iron (22-28 per cent Fe) and its basicity was 3.0-3.5.

In the examples discussed, steam-oxygen blow is applied during the whole process. Other techniques of blowing are also employed, for instance, the one by which oxygen-enriched air is blown in the first half of the melt and steam-oxygen mixture in the second.

The choice of a particular technique is decided by the technical and economical conditions of the shop. The same applies for the case when common open-hearth pig iron with 0.1-0.3 per cent phosphorus is to be converted with the application of steam-oxygen blow. This process is principally feasible, but one should keep in mind that in this case the deficiency in chemical heat will be compensated for by a greater oxidation loss of iron and a noticeably higher consumption of oxygen. In addition, the slag produced in this process cannot be utilized. The life of vessel bottoms will be reduced, but the productivity of converters will rise.

For instance, conversion pig iron of an analysis of 0.07-0.14 per cent P, 0.7-1.0 per cent Si, 0.7-1.1 per cent Mn, and up to 0.05 per cent S was used in 13-ton basic Bessemer converters at the Enakievsky iron and steel works, with steam-oxygen mixture being blown from the very beginning of the melt. The consumption of lime was 3.0-4.7 per cent of the mass of iron and that of oxygen, 45-60 m^3 per ton iron. The blow time was 6.7-8.8 minutes. The content of nitrogen in steel varied between 0.0015 and 0.0050 per cent and that of phosphorus, between 0.011 and 0.021 per cent.

Blowing with steam-oxygen mixture through the bottom of a basic Bessemer converter has the following advantages over top blowing with oxygen in a solid-bottom converter.

The formation of brown smoke during blowing is eliminated almost fully whereby the loss of iron carried off with converter gases is reduced. The process is easily controlled by varying the proportions of the components of the blow. The dust content of converter gases is 1 g/m^3, while in top blowing with oxygen the gases contain 30-70 g of dust per m^3. Therefore, the yield of final steel is greater.

Steam-oxygen blowing provides for a greater productivity owing to a shorter blow time. For instance, in experiments with 40-ton basic Bessemer converters blown with oxygen from above, the blow time was 22 minutes and the tap-to-tap time 45 minutes, while with steam-oxygen blow, all other things being the same, the blow time was 10 minutes and the tap-to-tap time 27.5 minutes.

Steam-oxygen blow can be used with success for conversion of any kind of pig iron into low-carbon steel to be rolled into automobile body sheets for deep-drawing. Only this method is capable of reducing the residual nitrogen content of steel to 0.0015-0.020 per cent.

Common pig iron of low phosphorus content may also be converted in acid Bessemer converters blown with steam-oxygen mixture. Experimental melts were made successfully at the Enakievsky iron and steel works with the steam-oxygen mixture (55-70 mass per cent O_2 and 30-45 mass per cent H_2O) blown during the whole melt. The composition of the blow varied with the composition of conversion iron (0.7-1.6 per cent Si). Up to 3 per cent iron ore was added to cool the melt. The average time of operation was 8.5 minutes against 12 minutes with air blowing. The life of the vessel and bottom lining and the yield of final steel were the same as with air blowing.

Tables 20 and 21 give the material and heat balances of a basic Bessemer melt blown with steam-oxygen mixture

Table 20

Material Balance of a Basic Bessemer Melt with Steam-Oxygen Blow (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kg		Output, kg	
Liquid iron	100.00	Steel	89.486
Tonnage oxygen	7.100	Slag	22.224
Steam	4.177	Iron beads in slag	1.000
Lime	11.585	Gases	10.752
Lining wear	1.600	Splashings	1.000
Total:	124.462	Total:	124.462

Table 21

Heat Balance of a Basic Bessemer Melt with Steam-Oxygen Blow (prior to deoxidation) per 100 kg of the Metallic Charge

Input, kcal (%)			Output, kcal (%)		
Physical heat of:			Enthalpy of:		
pig iron	24,660	(38.10)	steel	30,870	(47.70)
steam	3 140	(4.86)	slag	11,900	(18.40)
oxygen	31	(0.05)	converter gases[1]	6 297	(9.76)
Heat from oxidation of C, Si, Mn, P, and Fe	31,662	(48.96)	Heat for decomposition of lime	880	(1.36)
Slag formation	5 197	(8.03)	Steam dissociation	9 394	(14.50)
			Removed by splashed Fe_2O_3 particles	1 020	(1.58)
			Radiant and convective heat losses	3 165	(4.90)
			Surplus heat	1 164	(1.80)
Total:	64,690	(100.00)	Total:	64,690	(100.00)

---

[1] Of these on heating, kcal, (%): CO and CO_2, 3 435 (5.3); N_2, 100 (0.15); H_2, 1 700 (2.60); O_2, 74 (0.11); H_2O and SO_2 988 (1.60).

The heat balance shows that the amount of heat carried off with the converter gases is low, especially that due to nitrogen whose content in the gases is insignificant.

If the works is short in oxygen, other solutions are possible for intensifying the process and increasing the converter productivity. Experiments were carried out successfully by the scientists of the Moscow Institute of Steel and Alloys together with the engineers of the Dzerzhinsky iron and steel works, under the supervision of the author, in blowing a 22-ton basic Bessemer converter with mixtures of steam, oxygen, and air. Pig iron containing 0.9-1.1 per cent Si, 0.3-0.6 per cent Mn, 0.05-0.055 per cent P, and 0.035-0.045 per cent S was converted into rail and rimming steel. The time of operation was around 9 minutes when making rail steel and 10-11 minutes for rimming steel, against 17 and 15 minutes respectively with air blowing.

The content of hydrogen in the metal reached 5-6 cm^3 per 100 g. For that reason, the process of making rail steel was carried out with overblow: the melt at a high carbon content was blown with the mixture indicated for 6-8 minutes, then the vessel was turned down for sampling and after that the melt was blown during 1.0-1.5 minutes with oxygen-enriched air, or sometimes with atmospheric air. This method reduced the nitrogen content of the final steel at tapping to 4-3 cm^3 per 100 g. When making rimming steel, the melt was blown during the whole course of operation with the triple mixture, with the result that the final steel had the usual concentration of nitrogen.

Rail steel and rimming steel were made with the mixture composed of 25 kg steam, 35 m^3 oxygen and 175 m^3 air per ton of steel. It is natural that such proportions of blow components could not provide a noticeable reduction in the nitrogen content of the final steel.

As was established by control tests, in particular, impact tests, the rail steel produced by this method had its mechanical properties fully within the specifications. No flakes were found in it. The mechanical properties of the rimming steel (Grade Cт. 3кп) also were within the specifications. The life of bottoms and tuyeres was not lower than with air blowing. The temperature conditions were easily controllable during the melts and the converter gases were less dark than with air blowing.

BOTTOM BLOWING OF PIG IRON IN CONVERTERS WITH A MIXTURE OF OXYGEN AND CARBON DIOXIDE

Blowing pig iron with a mixture of oxygen and carbon dioxide is also aimed at reducing the pick-up of nitrogen by the metal and decreasing the nitrogen content of the final steel. As is known from the specialist literature, the final steel produced by this process contains 0.002-0.006 per cent nitrogen (0.0035 per cent in most cases), i.e., somewhat more than with steam-oxygen blow, but still less than with the common basic Bessemer process with air blow, in which the nitrogen content may reach 0.025 per cent.

A somewhat higher value of nitrogen in the steel produced by the process discussed may be attributed to the fact that carbon dioxide is usualy more contaminated with nitrogen than steam. It should be noted that carbon dioxide is rather costly and its production encounters certain difficulties (most often it is produced from combustion products of Cowper blast heaters). Melting may be done by one of the two methods as follows: (1) the mixture is blown through the metal during the whole course of the melt; or (2) the first half of the melt is run with oxygen-enriched air blow and the second half with the blow consisting of oxygen and carbon dioxide.

Figure 38*a* shows the variations in the composition of the blow and metal in the process of blowing of basic Bessemer pig iron with oxygen-carbon dioxide mixture during the whole operation. This method makes it possible to maintain the constant blow conditions during the whole melt, which are most suitable for the converter plug, eliminate splashings, and reduce the process time to a minimum.

But the process consumes 48 m^3 of oxygen and 60 m^3 of carbon dioxide per ton pig iron against 30 m^3 of oxygen and 30 m^3 of carbon dioxide in the operation by the second method.

A feature characteristic of the process is the behaviour of nitrogen. Its concentration decreases even when little carbon is left in the metal and the melt is heated up to a very high temperature.

Figure 38*b* shows the variations of the composition of the blow and metal in a basic Bessemer melt blown with oxygen-enriched air during the first half of the process and with oxygen-carbon dioxide mixture during the second half. The oxygen-carbon dioxide blow stops the pick-up of nitrogen by the metal. In melts with air blowing the metal usually becomes saturated with nitrogen in the second period of the process, and, besides, the main portion of the phosphorus is oxidized during overblowing. The tap-to-tap time in the second process is noticeably larger than in the first. Since the main object of this kind of blow is to reduce nitrogen content in steel, which also can be achieved by the less costly method of steam-oxygen blow, the latter is preferable over the former, unless there is some risk of impairing steel quality as regards its hydrogen content.

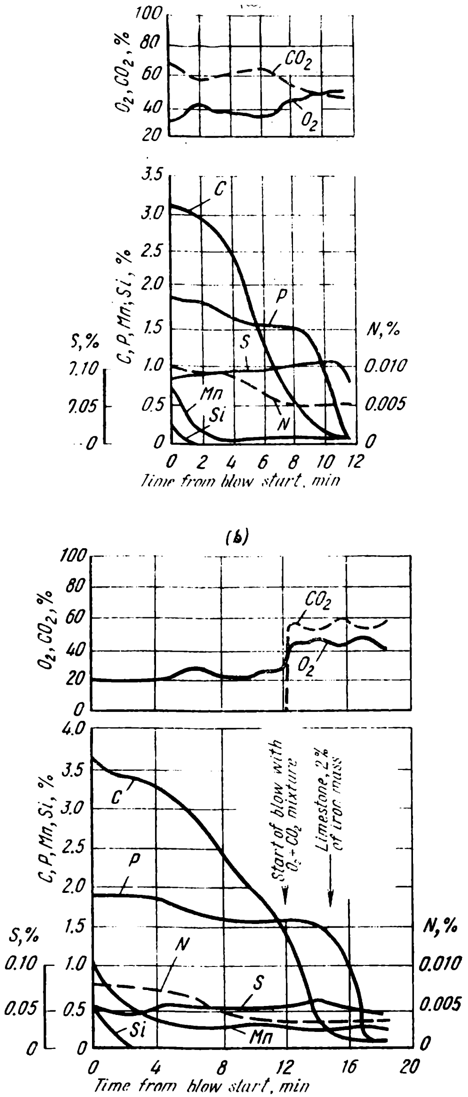

Fig. 38. Variations of compositions of the metal and blow in a basic Bessemer melt blown with ($CO_2 + O_2$) mixture

A—mixture blown during the whole operation; *B*—mixture blown during the second period only

TAPPING AND TEEMING OF ACID AND BASIC BESSEMER STEELS

The essential feature of the teeming of acid and basic Bessemer steels is that the whole melt of a relativiely low weight (19-22 tons) is teemed by bottom pouring into 4-6 moulds placed on a single bottom plate. For that reason the temperature of metal and the rate of teeming vary during teeming from their maximum to the minimum values. This has a certain detrimental effect on the internal structure of the top portion of ingots and promotes the formation of skin turns and surface defects. These drawbacks can be eliminated by direct pouring, but then the last ingot being cast turns out to have many surface defects.

When tapping a basic Bessemer converter, one has to remember that the slags of this process are much more free-running than those of the acid Bessemer process, so that there is a risk of their intermixing with the metal during tapping and of reversion of phosphorus from slag to metal. This is prevented by throwing lime and dolomite onto the surface of metal in the ladle so as to isolate and thicken the portion of slag passed into the ladle.

Modern oxygen-blown converters have a special notch for tapping metal, which ensures good separation of slag.

BESSEMER CONVERTER PROCESSES WITH BOTTOM BLOWING OF OXYGEN

Top blowing of a converter with oxygen inevitably entails large losses of iron with fumes and dust (more than 1.5 per cent of the mass of the metallic charge) because of a poor distribution of blow in the bulk of metal and poor hydrodynamics of the bath.

Studies were started long ago into remedying these drawbacks by supplying oxygen through the converter bottom via tuyeres or holes. An attempt to solve this problem industrially in 1936-1940 (O. Lellep, Mexico) was unsuccessful because of the hazard of explosions when using the suggested closed water nozzle cooling system in the converter bottom. In 1945-1946, V. V. Kondakov (USSR) worked on experimental Bessemer heats with oxygen supplied via tuyeres mounted in the converter bottom, but also without success because of the catastrophically rapid destruction of refractories in the high-temperature zones of oxygen supply.

In 1956, N. I. Mozgovoy et al. (USSR) employed for the purpose the method of direct cooling by a dissociating gas supplied through a coaxial-type tuyere, in which the inner copper tube 16 mm in diameter supplied oxygen under a pressure of 5 at, and the outer tube made of heat-resistant steel supplied an enveloping gas (carbon dioxide), at a pressure of 10 at. The annular clearance between the tubes was 0.75 mm. This method of direct cooling proved successful, since wear or damage of tubes could not be critical, and the cooling gas, which dissociated in the metal by endothermic dissociation reactions, was then partially regenerated in the bulk of metal owing to the secondary oxidation of the products of its decomposition. The method made it possible to supply oxygen into metal through the converter bottom, improved appreciably the hydrodynamics of the bath and the durability of the bottom, and reduced the loss of iron with fumes and dust.

Metallurgists in a number of countries, primarily in Western Europe where many basic Bessemer plants are in operation, have searched incessantly for suitable methods of industrially solving the problem, since the growing requirements on the quality of basic Bessemer steels could not be met any more even when melts were carried out with oxygen-enriched blow. Vast investigations have resulted in the development and industrial implementation of new processes of steelmaking in bottom-blown oxygen converters in Western Europe (OBM process, LWS process, QEK process) and in the USA (Q-BOP process). These processes attracted much interest in many countries: the German Democratic Republic, Belgium, Luxembourg, Sweden, the Republic of South Africa, the German Federal Republic, the USA, France. They were first realized at the existing basic Bessemer shops in 20-ton and 72-ton vessels for converting high-phosphorus pig irons. Besides, Bessemer shops with 150-ton vessels were built in Sweden and Belgium for oxygen bottom blowing of low-phosphorus pig irons. In Gary (USA), LD converters have been replaced with three 180-ton converters for conversion of low-phosphorus pig iron by the Q-BOP process and in Fairfield twelve 210-ton open-hearth furnaces will be replaced with bottom-blown oxygen converters for converting low-phosphorus pig iron by the Q-BOP process; three of them, of a size of 200 tons, are already in operation. Thus, four new processes have been developed. Let us discuss them separately.

The OBM Process

The OBM (Oxygen Boden Maximilianshütte) process was developed at the Eisenwerk Maximilianshütte in Sulzbach-Rosenberg (GFR) and first employed in 1968 for basic Bessemer conversion of pig iron (3.4 per cent C; 0.95 per cent Mn; 0.45 per cent Si; 1.7-1.8 per cent P; and 0.055 per cent S) in 25-ton vessels of a volume of 17 m^3. In view of the quiet course of melts, the charge of the vessels was later enlarged to 30 tons.

The detachable elliptical bottom of the converter carries, depending on the vessel size, 5 to 15 coaxial-type tuyeres disposed in one half of the converter bottom (Fig. 39*a*). This arrangement of tuyeres has proved optimal, since it ensures rapid melting of scrap, intense agitation of the bath, and the shortest blow time. As will be seen from the Figure, each tuyere has an inner tube to supply oxygen and powdered lime and an outer tube which forms an annular passage for the supply of a protective gas. As the vessel is tilted down, the tuyeres emerge from the molten metal. During the charging of steel scrap, the vessel is turned still lower, so that even lagre lumps of scrap cannot reach the tuyeres.

Oxygen in supplied at a pressure of 10 at, its jets being enveloped by propane gas (C_3H_8) supplied at a pressure of 6 at. At this plant all the lime specified for the melt is introduced as powder into the oxygen jet. At other works, where this method of lime addition has not been mastered, lump lime is charged into converters. In conversion of high-phosphorus pig iron, 695 kg of liquid pig iron and 400 kg of steel scrap are charged per ton of steel produced.

After the first blow, the vessel is turned down, the phosphate slag is run off, and a new portion of lime is charged, or blown with oxygen for 1 minute on turning up the vessel. During this time, a new slag of a basicity of 4.2 is formed, which is quite sufficient for deep dephosphorization

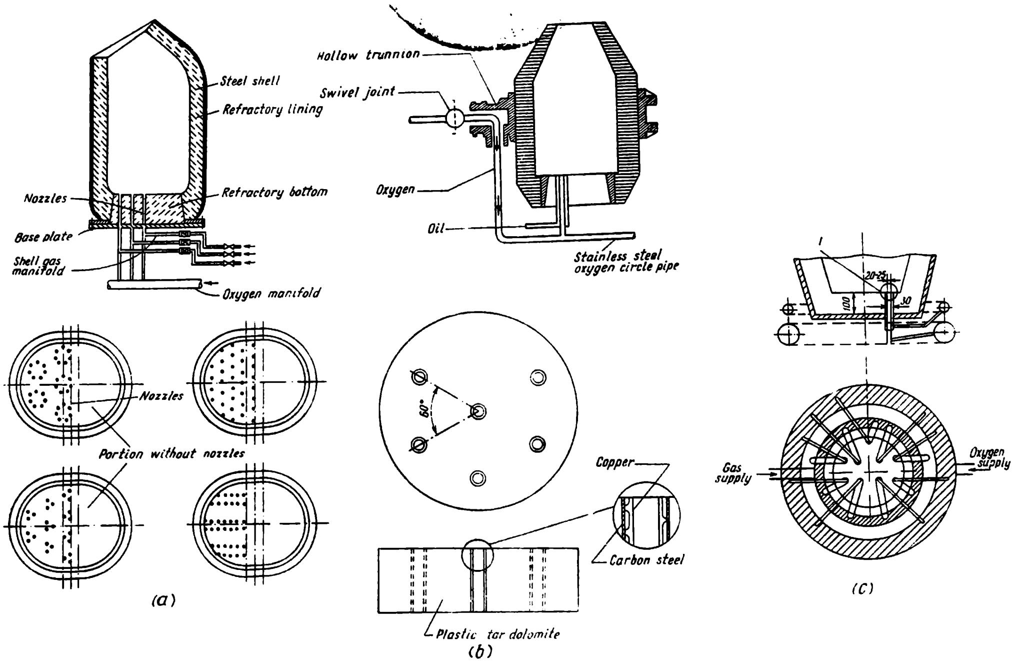

Fig. 39. **Diagrams of supply of oxygen and protective gas (or liquid fuel) and layout of nozzles in** (*a*) OBM process, (*b*) LWS process, and (*c*) Q-BOP process

and desulphurization of the metal (down to 0.03 per cent for each element). When making steel grades for which lower concentrations of P and S are specified, the process is run with an additional slagging-off and adjustment of new slag, this operation being usually done at 0.04 per cent C and 0.08 per cent P in the melt. The final blow continues for one minute with a large amount of lime supplied to the blast. The total consumption of lime in the melts reaches 125 kg per ton of steel. The consumption of lime and the blow time are reduced by 25 per cent when lime is blown in with oxygen.

The concentration of hydrogen dissolved in the metal increases at the end of the heat and reaches 7-10 cm^3 per 100 g of metal owing to dissociation of the protective hydrocarbon gas. It has been reported that for certain grades of steel the concentration of hydrogen is lowered by blowing a washing gas (nitrogen or argon) through the metal at the end of the operation for 30-45 s to reduce hydrogen concentration to 2-2.5 cm^3 per 100 g of metal.

The bottom tuyeres are sometimes used for preheating the scrap charged in the vessel. The amount of scrap per ton of steel produced at the works is usually 280 kg, but can be raised to 400 kg by preheating it during 12 minutes. The vessel is lined with magnesite or dolomite bricks to a thickness of 350 mm. The life of the vessel lining is about 400 melts and the life of rammed or lined bottoms now reaches 300 melts.

As stated by the Eisenwerk Maximilianshütte, the OBM process has a number of advantages over the LD-AC process, in particular, by the following parameters given below:

	LD-AC Process	*OBM Process*
Converter capacity, tons	22	30
Blow time, minutes	25	12
Yield of final steel, %	85	90
Life of 350-mm lining, melts . . .	100	450

With the transfer of the plant to operation on 30-ton converters by the OBM process, the output of steel has been raised from 55,000 to 80,000 t per month and its quality improved, in particular, as regards its nitrogen content.

When converting high-phosphorus pig iron by the OBM process, the elements are burnt out in the same manner as in the basic Bessemer process and the melt has a characteristic overblow period during which most of the phosphorus is oxidized. But the duration of the periods and the tap-to-tap time are shorter in this process, since the slags of the OBM process contain much less iron oxides FeO than common basic Bessemer slags, which can only be explained by the fact that the metallic and slag phases undergo intensive intermixing in the OBM process owing to a uniform distribution of the oxidizing blow and a characteristic hydrodynamics of the bath. Of considerable importance in speeding up the melting is the intensive action of oxygen jets on the process of smelting of even large lumps of steel scrap charged into the vessel.

The OBM process is also applicable for conversion of low-phoshorus pig irons and production of low-carbon steels with a phosphorus content below 0.03 per cent. In melts for medium-carbon steel and even for steels of 0.7 per cent carbon, it is possible to reduce phosphorus content below 0.02 per cent, but only when powdered lime is blown with oxygen. Since the conversion of low-phosphorus pig irons is done without overblow, no excessive saturation of the metal with hydrogen is observed. The steel at tapping contains 2.5-3.5 cm^3 hydrogen per 100 g of metal. It is possible to reduce the hydrogen content to 1.2-1.8 cm^3 by short washing of the metal with nitrogen or argon. Washing of the bath with an inert gas can probably be used to control decarbonization and thus reduce the carbon content of the metal, when needed, to 0.03 per cent or even 0.01 per cent.

Thus, as compared with the basic Bessemer process, the OBM process ensures a shorter blow time, smaller loss of iron with fumes and dust, a quiet course of the operation without splashings, the possibility of using vessels of a smaller unit volume, a higher percentage of scrap in the charge (35 per cent against 18 per cent in the basic Bessemer process with oxygen-enriched air blow), a longer life of bottoms, a higher yield of steel (by 2 per cent or more), a lower nitrogen content of the steel produced (0.004-0.006 per cent), and the possibility to use large-size scrap.

The LWS Process

The LWS (Loire-Wendel-Sidelor) process was developed in France at about the same time as the OBM process in the GFR. Steam and carbon dioxide were initially used in this process to protect oxygen jets and later were replaced with liquid fuel (fuel oil). The experiments were carried out in a 24-ton converter of a volume of 26 m^3. Melting was done with the charges up to 30 tons. The diagram of the converter and the arrangement of tuyeres in its bottom are shown in Fig. 39*b*.

The inner copper tubes supply oxygen and the narrow annular passages between the inner and the outer tubes, liquid fuel. The outer tubes are inserted in the converter bottom during its preparation, and the inner tubes just before starting the converter operation.

The oxygen-supplying pipeline provided with a non-return valve passes through a hollow trunnion of the vessel to a circle pipe near the bottom. The latter pipe communicates with the copper oxygen tubes via flexible hoses. Liquid fuel is pumped to the tuyeres via an individual pipeline provided with a control valve, flowmeter, and non-return valve. The non-return valves can automatically switch over from supplying oxygen and fuel to air supply. The pressure of oxygen in the pipelines is 12 at, that of fuel 11 at, and that of air 2 to 9 at.

The process in the vessel occurs quietly, without splashing. The life of the tar-dolomite bottom 900 mm thick is 400-500 heats, sometimes 600 heats, and equals the life of the vessel lining which is also made from tar-dolomite brick. Refractories are spent in an amount of 5 kg per ton of steel. Attaching the bottom to the vessel requires eight hours and its removal at the end of the campaign, 4 hours. The vessel can be relined in 3-3.5 days.

The charge for conversion of common basic Bessemer pig iron is 71 per cent iron and 29 per cent steel scrap. The consumption of oxygen is 64 m^2 per ton steel, including 4 m^3 spent to burn the fuel supplied at a rate of 3.5 litres per ton steel. The phosphate slag on skimming contains 18 per cent P_2O_5 and 16 per cent Fe (total iron).

The blow time, which is within 7-10 minutes, and the yield of steel depend on whether the metal is cooled with iron ore or scrap, and also on the size of scrap. Sometimes CO_2 is added to the blow in the last two minutes of blowing and the metal is washed from hydrogen by nitrogen or air blown in the last minute. The hydrogen content of the metal is usually 5.5-9.0 $cm^3/100$ g before final blowing and 2.8-3.9 $cm^3/100$ g after it. The steel is rather fine from impurities: 0.025 per cent P, 0.015 per cent S, and 0.0025-0.0035 per cent N_2, and its yield is 90 per cent. The cost of steel is the same as in the basic Bessemer process.

The works uses the process for treating common low-phosphorus pig iron, with 26 per cent scrap in the charge. As is claimed, the proportion of scrap can be raised to 33 per cent by using larger vessels (owing to lower unit heat losses).

The LWS process has not yet found application outside France.

The QEK Process

Experiments were carried out at the Maxhütte works of the VEB Qualitäts- und Edelstahl-Kombinat in Unterwellenborn (GRD) back in 1958 on bottom blowing of basic Bessemer pig iron in 100-kg and 6-ton vessels. Industrial heats in a 20-ton converter were started in 1969. Upon construction of an oxygen plant in 1974 the basic Bessemer shop of the works was fully rearranged for operation by the new QEK process (the name derived from Qualitäts- und Edelstahl-Kombinat). The output of the shop and the life of converter bottoms were thus increased appreciably.

The QEK process is very much like the OBM process. The protective medium here is liquid fuel oil too. The bottom of the vessel has 8 tuyeres supplied with oxygen from a circle manifold. The diameter of the oxygen-supplying copper tubes is 24 mm, and the annular gap between them and the outer fuel-supplying tubes is 0.7 mm wide. The consumption of oxygen (at a pressure of 10 at) is 64 m^3 per ton of steel, and that of fuel oil (4 at), 3.7 kg per ton of steel. The charge used is common high-phosphorus pig iron and scrap (180-280 kg scrap per ton steel). The blow time is 13.5 minutes. The process is run with one slag, the slag produced being of standard commercial quality. The final metal contains

0.01-0.03 per cent carbon, 0.1-0.2 per cent manganese, 0.03-0.05 per cent phosphorus, 0.02-0.03 per cent sulphur, and roughly 0.005 per cent nitrogen. The heats are done with a characteristic overblow period. The contents of sulphur and phosphorus in the steel produced may be considered rather low, regarding the fact that the shop operates as yet with lump lime. As in the LWS process, the content of hydrogen in the metal can be reduced here to normal levels with nitrogen blown for 30-50 s at a flow rate of 2-3 m^3 per ton of steel.

The Q-BOP Process

Extensive experiments were carried out at the South-Chicago works of the United States Steel Co., USA, in 1971 on treating low-phosphorus pig iron in a 27-ton bottom-blown oxygen converter. Powdered lime was added to oxygen jets to attain a reasonable degree of dephosphorization. Various designs of the vessel and layouts of tuyeres were tested. The coolant was natural gas: methane (CH_4) or propane (C_3H_8). Experimental heats, 337 in all, were performed to work out the process technology, including overblow at a given carbon content, as also the technique of blowing in the lime. The experiments resulted in industrial implementation of the new Q-BOP (quiet basic oxygen) process.

Figure 39*c* shows a possible diagram of gas supply through the vessel bottom and the layout of tuyeres for the supply of oxygen, protective gas, and lime. The company soon decided to replace 12 open-hearth furnaces at their works in Fairfield with bottom-blown oxygen converters for operation by the new process. Two Q-BOP converters of a capacity of 200 t are already in operation and treat low-phosphorus pig iron. The expected capital expenditures on reconstruction of an open-hearth shop are reportedly lower by 50 per cent than the cost of building of a new LD shop of the same output.

At another works of the same company in Gary, three Q-BOP converters of a capacity of 180 t for treating low-phosphorus pig iron were installed instead of planned LD converters. The shop was put into operation in 1973. As is reported, each converter in the shop is covered by a hood to collect fumes, the doors of the hood being opened only during charging.

Even at the stage of developing the process conditions, the operational characteristics of Q-BOP converters as compared to LD converters of the same capacity were as follows:

	Q-BOP	*LD*
Charged per ton of ingots:		
metallic charge, kg	1147	1176
lime, kg	56	66
dolomite lime, kg	18	23.5
fluorspar, kg	4	5
oxygen, m³	47.5	50
nitrogen, m³	21.4	—
natural gas (methane), m³	5.25	—
Maximum life of lining, melts:		
bottoms	375	No data
vessel	840	

The tap-to-tap time is 31-41 minutes, of which 11-13 minutes fall on blowing. The highest productivity of a converter was reported to be 14 heats in an 8-hour shift, with only one heat done with overblow. This is evidence that the process is easily controllable. It is possible to melt heavy pieces of scrap (up to 25 tons) in Q-BOP converters, in particular large-size rejected ingots, because of the strong cutting action of oxygen jets. It is appropriate to note that in the LD process pieces of scrap of a size more than 300 mm sometimes remain unmelted by the end of the heat. The charge at the Gary works contains 36 per cent scrap, or even 45 per cent when scrap preheating is resorted to.

The Q-BOP process produces steel fine in impurities: 0.003-0.005 per cent nitrogen, not more than 0.025 per cent sulphur, and not more than 0.01 per cent phosphorus for low-carbon steels (or 0.025 per cent P for steels containing 0.11-0.50 per cent C). Such good indices of dephosphorization and desulphurization are ensured by introducing 45 per cent of the required amount of lime in powdered form with oxygen, the remainder being lump lime charged into the vessel.

The manganese content of the metal before tapping is usually 0.10-0.15 per cent higher than in the LD process, and therefore less manganese is needed for deoxidation of steel. This is because the slags are less oxidized. Even at the moment when the carbon content of the metal is 0.15-0.20 per cent, the FeO content of the slag does not exceed 5-7 per cent, i.e., is lower by a factor of two than in the process with oxygen top blowing.

At the end of melting, in the last 30-40 seconds, the metal is washed from hydrogen by blowing an inert gas or nitrogen. The same technique is used, when needed, for very deep decarbonization.

These converters are also used with success to treat low-phosphorus pig iron with overblow at a given carbon content. A general diagram of supply of reagents for the Q-BOP process is shown in Fig. 40.

Exhaustive studies carried out at some works have shown that the quality and operational characteristics of various grades of steel, including special steels, made by the Q-BOP process can fully satisfy the standards and technical specifications.

Thus, having discussed briefly the processes of steelmaking in bottom-blown oxygen converters, their technological possibilities can be evaluated as follows:

1. Supplying oxygen into metal in the form of jets enveloped by gas or fuel oil fed at a high pressure shifts the high-temperature centres of reactions farther from the bottom lining and from the ends of tuyeres. At the same time, the endothermic reactions of dissociation of hydrocarbon fuel and of its combustion products lower the temperature of the centre of the initial reaction so that even small formations of skull can appear on the bottom in the tuyere zone. These conditions are favourable in increasing the life of the bottom lining and decreasing dust formation and evaporation of iron, thus reducing the loss of iron with fumes.

2. The protective gas, supplied in an amount of 6-9 per cent of oxygen, acts mainly as a coolant when penetrating the metal, but burns out in the upper layers of the bath. The heat brought in through its combustion is sufficient to increase the percentage of scrap in the charge up to 36-42 per cent.

3. Iron oxide and dust formed in the lower layers of the bath through partial evaporation of iron are filtered and

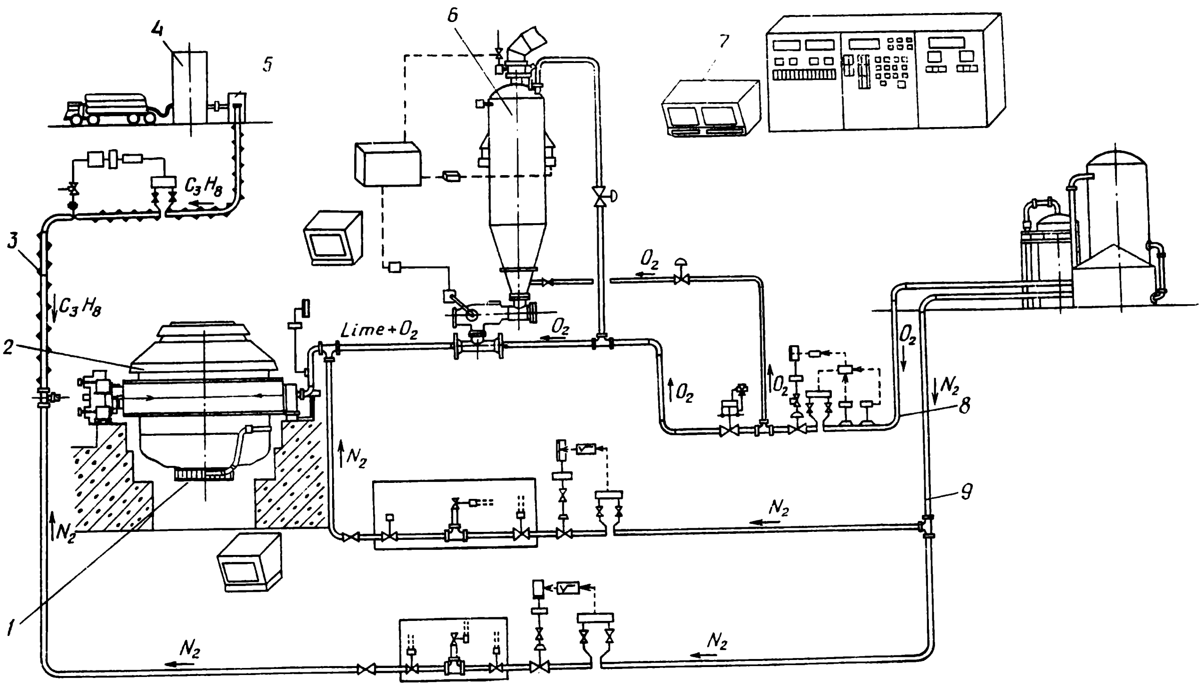

Fig. 40. General diagram of a bottom-blown converter with arrangements for supply of lime and gases

1—tuyeres; 2—converter; 3—propane pipeline; 4—propane reservoir; 5—evaporator; 6—lime bunker; 7—control panel; 8—oxygen pipeline; 9—nitrogen pipeline partially picked up by the metal as they move upwards. For that reason the waste gases of the Q-BOP process carry off less dust than in the LD process.

4. Iron oxides formed in the reaction zone, when passing to the slag through the column of metal, are partially assimilated through their decomposition, (FeO) → [O] + [Fe], so that only a small amount of FeO (roughly 5-9 per cent) is picked up by the slag. This has an adverse effect on the rate of dissolution of lime (if lump lime is used) and on the reactions of dephosphorization in the metal. For that reason, powdered lime should be employed in the oxygen converter process, this being blown in with oxygen via tuyeres.

5. Owing to a larger percentage of scrap in the charge and a lower loss of iron with slag, fumes, and dust, the yield of final steel in the process is greater by 2.5 per cent or even more than in the process with top blowing of oxygen.

6. The quiet course of the process, without splashing, makes it possible to employ vessels of a smaller volume for a given weight of the charge. The charge of existing basic Bessemer converters can be increased on transferring them to oxygen bottom blow if the load-carrying capacity of the teeming crane permits it. An essential feature of the process is a short blow time, which however is sufficient to melt even large-size scrap; this is favoured by a good hydrodynamics of the bath and cutting effect of oxygen jets.

7. The process ensures a high productivity. It is most suitable for making low-carbon steel rather fine from impurities. But low-phosphorous pig iron can also be treated for medium-carbon grades of steel, with the process run with overblow at a specified carbon content.

8. The steel produced has low concentrations of phosphorus, sulphur, and nitrogen. An excessive content of hydrogen in the metal at the end of the heat can be easily normalized by a short blow of nitrogen or argon.

9. Q-BOP converters can be installed in existing open-hearth shops in place of furnaces, which makes it possible to employ the existing equipment for charging, iron pouring and teeming (see Fig. 127). But deep trenches near converters are indispensable.

10. A process has been tried in Canada, by which oxygen enveloped by a protective gas is supplied together with lime

into the bath of a 220-ton open-hearth furnace through its rear wall with the purpose of deep blowing of metal. The process has been called the SIP (submerged injection) process. It enables a tremendous amount of oxygen to be blown into the bath via a few tuyeres during a very short blow period. The tap-to-tap time has thus been reduced from 8 hours to 3 hours and even 1.5 hours. The process has been attempted in the USA and the USSR, but so far has not found wide application.

A disadvantage of the oxygen-converter process with bottom blowing is that a special shop should be provided for preparation of converter bottoms. Another drawback is that the system for supplying powdered lime and four various gases (oxygen, protective gas or liquid fuel, inert gas, and air) is very complicated in maintenance. At the time of developing the process, the American metallurgists used to say, not without reason, that the converter bottom is a perfection for a fitter and nightmare for a repairman. The problem of capture of splashed metal and slag during converter tilting still remains unsolved. Deep trenches near converters create some inconveniences in the organization of work.

Chapter Seven

SMALL BESSEMER CONVERSION

Small Bessemer conversion is the process of treating pig iron in side-blown converters (Fig. 41) of a small capacity (1-10 t, most often 1.5-3.0 t). The inner layer of the vessel lining is made from silica brick (or quartzite), and the outer layer from fireclay brick.

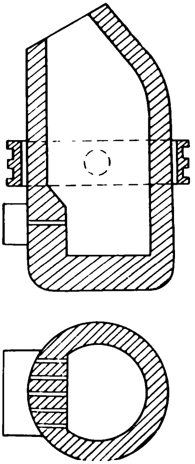

Fig. 41. Side-blown small Bessemer converter

The process uses chemically hot iron containing 1.26-1.75 per cent Si, 0.6-1.2 per cent Mn, not more than 0.07 per cent P, and not more than 0.04 per cent S. Pig iron is usually smelted with a small amount of scrap in a cupola furnace and then poured into the vessel at a temperature above 1300°C (before pouring, the pig iron may sometimes be pretreated with soda for desulphurization).

Air at a pressure of 1.25-1.40 at and a flow rate of roughly 500 m^3 per ton iron is introduced into the bath to a small depth below its surface via a row of 5 to 8 nozzles mounted in the thickened portion of the vessel lining near the wind box. The diameter of a nozzle is 30-50 mm. One of the trunnions of the vessel is hollow for passing blast air, so that the vessel can be turned through 5-15 degrees from the vertical in any direction without stopping the blow; this tilting makes is possible either to blow through the metal or to direct the air onto the metal surface.

During the first period of the melt, the metal is blown to effect heating, mixing, and circulation when mainly the reactions of oxidation of silicon, manganese and partially of iron occur in the metal.

The slag is formed from the oxides in the bath and through partial dissolution of the lining. The impurities left in the bath can also be oxidized through direct interaction with the slag. At the same time reactions of neutralization occur between the acid and basic constituents of the slag. The metal is heated up by the heat evolved through oxidation of impurities and the heat of slag formation: its viscosity reduces to a value required for starting the second period.

During the second period, carbon is oxidized intensively by the oxygen of the blow and the dissolved oxygen by the reactions

$$[\mathrm{C}] + 0.5\{\mathrm{O_2}\} \rightarrow \{\mathrm{CO}\}$$

or

$$[\mathrm{C}] + [\mathrm{O}] \rightarrow \{\mathrm{CO}\}$$

Bubbles of carbon monoxide intensify mixing and circulation in the bath. The vessel is then turned down to direct the blow onto the bath surface for afterburning the carbon monoxide evolved by the reaction

$$\{\mathrm{CO}\} + 0.5\{\mathrm{O_2}\} \rightarrow \{\mathrm{CO_2}\}$$

which brings in additional heat to the bath. This is of large importance for melts carried out in small-size converters. Decomposition of silicates then begins in the slag by the reaction

$$(\mathrm{FeO})_x \cdot \mathrm{SiO_2} = x\mathrm{FeO} + (\mathrm{SiO_2})$$

and the additional FeO passes from slag to metal: $(\mathrm{FeO}) \uparrow \rightarrow [\mathrm{FeO}]$. This speeds up carbon oxidation. Because of the evolution of numerous bubbles, the bath foams and rises well above the level of the nozzles, so that the blow is again done through the metal, rather than over its surface, and no additional heat from afterburning CO into $\mathrm{CO_2}$ is now available.

This partial chilling of the process results in lowering the rate of carbon oxidation. Now the passage of oxygen from the slag to metal is suspended, since the reactions of thermal decomposition of silicates cease or slower down. All this results in the metal surface sinking to the initial lower level, so that the blow again strikes the metal surface and the whole cycle is soon repeated. When the bath is deficient in heat, the intensity in oxidation of silicon and manganese increases. The third period of blow is not clearly pronounced in this process.

Thus, as with bottom-blown converters, there are two zones of oxidation of impurities in a side-blown converter, i.e., the blast zone and the circulation zone. In the blast zone, all impurities are oxidized at the blow surface, but the intensity of oxidation depends on the affinity of an element for oxygen at a given temperature. Because of a low rate of diffusion of impurities and of poor mass transfer, atoms of iron are oxidized in a great amount, so that the small volumes of slag and metal confined to this zone are saturated respectively with ferrous oxide and oxygen. The remaining volume of the bath, farther away from the blast zone, is the circulation zone where secondary reactions occur. The cycle and sequence of oxidation reactions and slag formation are the same as with bottom blowing.

The unit loss of heat in small-size converters is appreciably greater (up to 10-14 per cent of the total heat supplied) than in large converters, since the area of heat transfer per ton of metal is much larger. For that reason chemically hot pig iron heated up to 1380°C before pouring must be used in the process. In cases when the converter lining cools appreciably between melts, exothermic additions, in particular, 45 per cent ferro-silicon must be made during melting. The diagram of such a cold melt is shown in Fig. 42.

In the Russian version of small Bessemer conversion, the temperature of the converter lining reaches 1400-1500 °C and that of pig iron at pouring, 1400-1450°C, though a low-silicon metal (up to 1 per cent Si) is usually employed. This ensures a sufficiently hot run of the melt, so that no additions of ferro-silicon are needed.

The amount of nitrogen dissolved in small Bessemer steel is 0.005-0.008 per cent, i.e., much lower than in basic Bessemer steels. This can be explained by a different method of blasting, lower blast pressure, smaller area of contact between blow and metal, and a shorter path of blow in the bath. The steel is also noticeably lower in non-metallic inclusions, which is due to lesser disintegration of the slag and the existing uprising currents favouring the removal of emulsified slag particles from the metal to the slag phase.

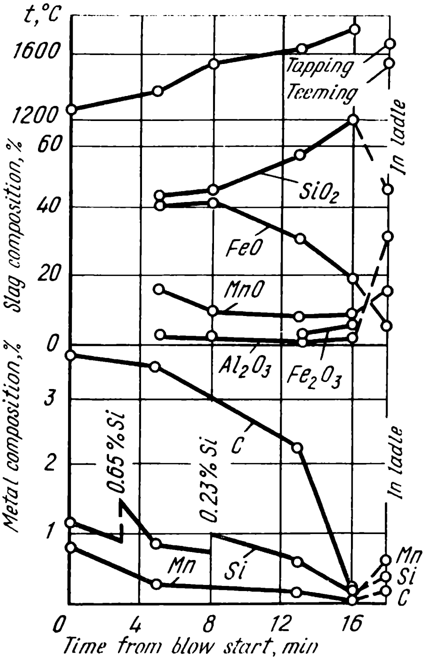

Fig. 42. Diagram of a cold melt by the small Bessemer conversion process

Because of its low content of inclusions, the steel is appreciably more fluid than is the usual steel, which is of large importance for making steel castings. The technico-economical indices of the process are affected by a high oxidation loss of metal (12-15 per cent) and a low yield (84-86 per cent).

Further improvements of the process follow the path of intensification with oxygen. By using oxygen-enriched air (up to 40 per cent O_2), the tap-to-tap time has been substantially reduced, both for acid and basic small Bessemer converters.

Apart from the common merits of oxygen-enriched air blow (reduction of nitrogen content of steel to 0.004-0.006 per cent) or pure oxygen blow (to 0.002-0.004 per cent nitrogen), the use of oxygen in small side-blown Bessemer converters improves the heat balance, which makes it possible to add less ferro-silicon to the melts, and in some cases, to use scrap in an amount of up to 15 per cent of the mass of the metallic charge. This increases the yield of steel and reduces the cost of casting.

In the Chinese People's Republic, pig irons containing 0.15-0.35 per cent phosphorus and high-phosphorus pig irons (1.2-1.8 per cent P) are converted into steel for steel castings and ingots in side-blown basic turboconverters, with the air blow enriched to 27-30 per cent O_2. The blow pressure is 1.5 at. The turboconverter (Fig. 43), of a capacity of 1.5 to 7.0 t, is of a pear shape with a large working space above the metal level, the unit volume of the vessel reaching 1.0. This shape ensures intense mixing of the slag, metal and gaseous phases. A strong circulation in the bath favours quick oxidation of impurities and afterburning of CO to CO_2, i.e., adds more heat to the process.

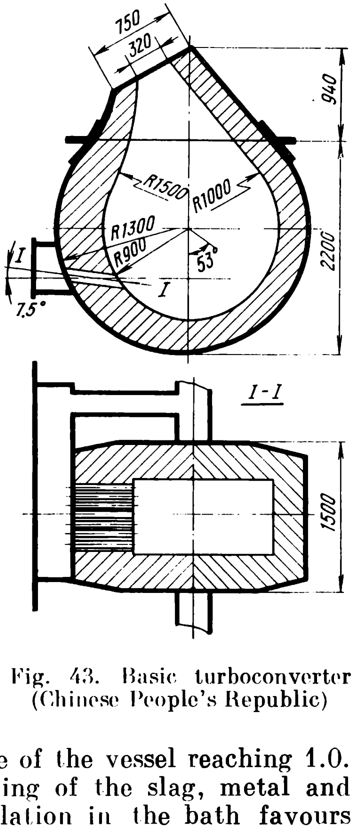

Fig. 43. Basic turboconverter (Chinese People's Republic)

When treating high-phosphorus pig irons in turboconverters, the final slag of the previous melt is left in the vessel, which makes it possible to obtain commercial phosphate slag with 14 per cent P_2O_5. A graph of blowing high-phosphorus pig iron in a turboconverter with oxygen-enriched air is shown in Fig. 44. The high intensity of oxidation of phosphorus is due to an early formation of slag as a result of vigorous passage of ferrous oxide to slag, accelerated dissolution of lime owing to the additional heat evolved in the bath through afterburning of CO to CO_2, and intense circulation and mixing of metal and slag in the top portion of the turboconverter.

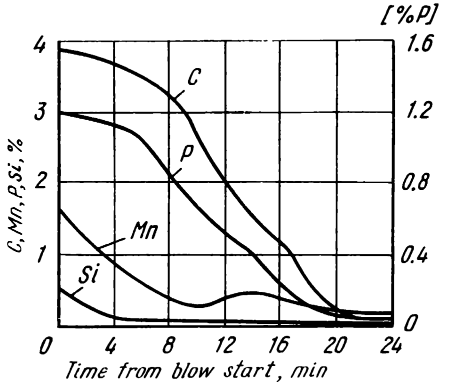

Fig. 44. Variations of composition of metal (high-phosphorus pig iron) during blowing in a basic turboconverter (Chinese People's Republic)

As will be seen from the Figure, at the moment when carbon content drops down to 0.5 per cent, the steel is very low in phosphorus, so that no overblowing is needed.

With the air blow enriched to 27 per cent O_2, the nitrogen content of the final steel is within 0.0045-0.0060 per cent. The steels produced by the process have satisfactory mechanical properties especially as regards their impact strength at low temperatures.

Chapter Eight

OXYGEN CONVERTER PROCESSES

DESIGN AND LINING OF OXYGEN CONVERTERS

The Plant. When designing oxygen converters of a large capacity, their parameters are selected empirically, since the theoretical principles relating their shape with the aero- and hydro-dynamic phenomena occurring in them during the blow have not yet been developed.

In most cases, an oxygen converter is given a pear-like shape with a concentrically positioned throat, which ensures the best conditions for pouring in pig iron and charging scrap. The shell of the throat is sometimes made of pig iron with cast-in pipes for water cooling; the life of the throat thus increases and, in addition, it clears well from metal and slag skulls.

Modern oxygen converters are mainly designed for capacities of 100, 150, 180, 250, 300, and 350 t. Figure 45 shows sections through various large-size converters. All of them have a spherical bottom, cylindrical middle portion, and frusto-conical throat.

The shape of modern converters is selected depending on their capacity and the specified rate of oxygen supply for a melt. For a given distance from the end of the lance to the surface of the quiet bath, and a given pressure and flow rate of oxygen, the diameter of the cone of the oxygen jet at the point of striking the metal surface can be determined. One also has to consider that the lance must be positioned sufficiently high to ensure the formation of ferruginous slags which accelerate dissolution of lime. In this way one can find an optimum inner diameter of the vessel for specified melt conditions and the life of the lining.

A normal course of melt without much splashing is possible if the minimal allowable inner volume of the vessel has been chosen correctly. Splashing can be reduced appreciably

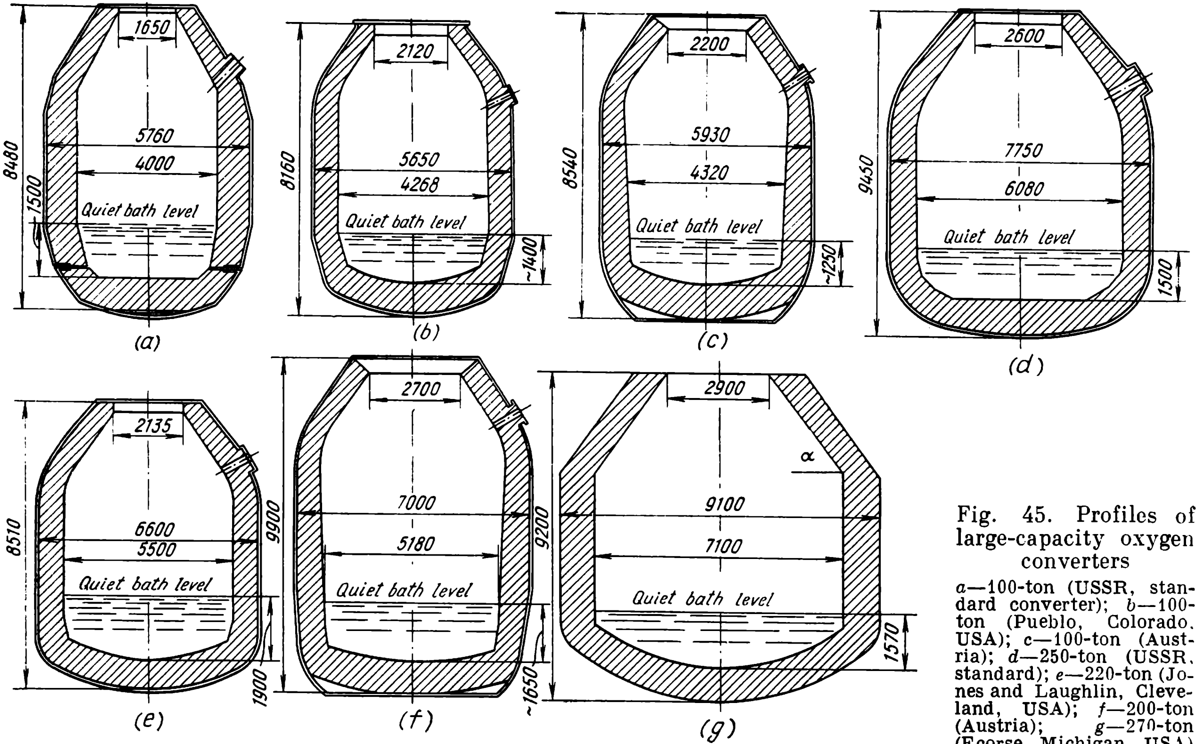

Fig. 45. Profiles of large-capacity oxygen converters

a—100-ton (USSR, standard converter); *b*—100-ton (Pueblo, Colorado, USA); *c*—100-ton (Austria); *d*—250-ton (USSR, standard); *e*—220-ton (Jones and Laughlin, Cleveland, USA); *f*—200-ton (Austria); *g*—270-ton (Ecorse, Michigan, USA) by using multi-nozzle lances. This enables larger vessels having a smaller unit volume to be employed. Thus, for instance, the unit volume of small vessels of 50 to 100 tons varies within 0.80-1.10 m^3/t, but is lower (0.80-0.85 m^3/t) for medium-size converters of 120-130 tons and still lower (0.70-0.79 m^3/t) for large converters of a capacity of 270 and 300 tons and more (see Table 22).

Table 22

Principal Parameters of Oxygen Converters

Parameter	Type (see Fig. 45)						
	a	*b*	*c*	*d*	*e*	*f*	*g*
Capacity, t	100	100	100	250	220	200	270
Total height *H*, mm	8480	8160	8540	9450	8510	9900	9200
Maximum diameter, *D*, mm	5760	5650	5930	7750	6600	7000	9100
H : *D* ratio	1.47	1.45	1.44	1.22	1.29	1.42	1.01
Diameter of bath, *d*, mm	4000	4260	4320	6080	5050	5180	7100
Depth of bath, *h*, mm	1500	1420	1250	1500	1900	1650	2570
Unit volume, m^3/t	0.8	0.79	0.85	0.78	0.66	0.93	0.70
Unit surface area of bath, m^2/t	0.126	0.143	0.146	0.116	0.090	0.105	0.146
Throat diameter, mm	1650	2120	2200	2600	2135	2700	2900

The selection of the unit volume of converters is determined by the process technology adopted in the shop. With the use of scrap as a coolant the unit volume of converters is taken smaller than with iron ore. The latter, when added, may be the cause of intense splashing if the vessel's unit volume is too small. When a larger unit volume is required for a given diameter of the vessel, a larger *H* : *D* ratio must be assigned, that is, the height of the vessel must be increased. This will diminish splashing, but cause extra capital expenditures for the construction of the stage of the converter bay and the dust-collecting chimneys, necessitate the use of longer oxygen lances and a more powerful mechanism for converter turning, and complicate sampling of metal.

With a smaller $H : D$ ratio, it is possible to install larger converters in shop buildings of the same height as for 100-ton converters, which can reduce appreciably the total capital expenditures.

As follows from the data of Table 22, vessels of larger capacities have a greater inner diameter and a lower $H : D$ ratio. But the amount of splashing is mainly determined by the distance from the bath surface to the throat, i.e., by the height of the free space in the vessel. This parameter may vary within 5.51-8.78 m for converters from 100 to 300 tons.

With a larger inner diameter of the vessel the life of the lining increases, especially when the lance is carefully centred in the vessel by means of special devices.

In practice, the relationships between the vessel capacity, inner diameter, and depth of the bath are as follows:

Capacity, t	*Inner diameter*, m	*Bath depth*, m
50	3.2-3.4	1.05-1.10
100	4.0-4.4	1.40-1.50
150	4.8-5.5	1.54-1.61
180	5.4-5.52	1.63-1.71
200-210	5.5-5.94	1.85-1.90
270	6.4-6.91	1.57-1.71
300	6.71	1.99-2.05

When designing a new converter, the ratio of its diameter to the depth of the bath is taken from 3.0 to 3.6 (in operating converters, this ratio is between 2.0 and 5.0), and the unit surface area of the bath, from 0.13 to 0.16 m^2 per ton steel.

The diameter of the throat is determined from the weight of scrap to be charged for melting. The more scrap is to be charged during the short time specified, the wider the charging scoop must be, and therefore the wider must be the throat of the vessel. On the other hand, too large a diameter of the throat may be the cause of suction of atmospheric air into the vessel during oxygen blow in the uppermost position of the lance. This can result in an increased concentration of nitrogen in the final steel. In existing converters, the diameter of the throat is 0.52-0.63 of the inner diameter of the vessel (1.6-3.8 m). In converters of latest design, even of

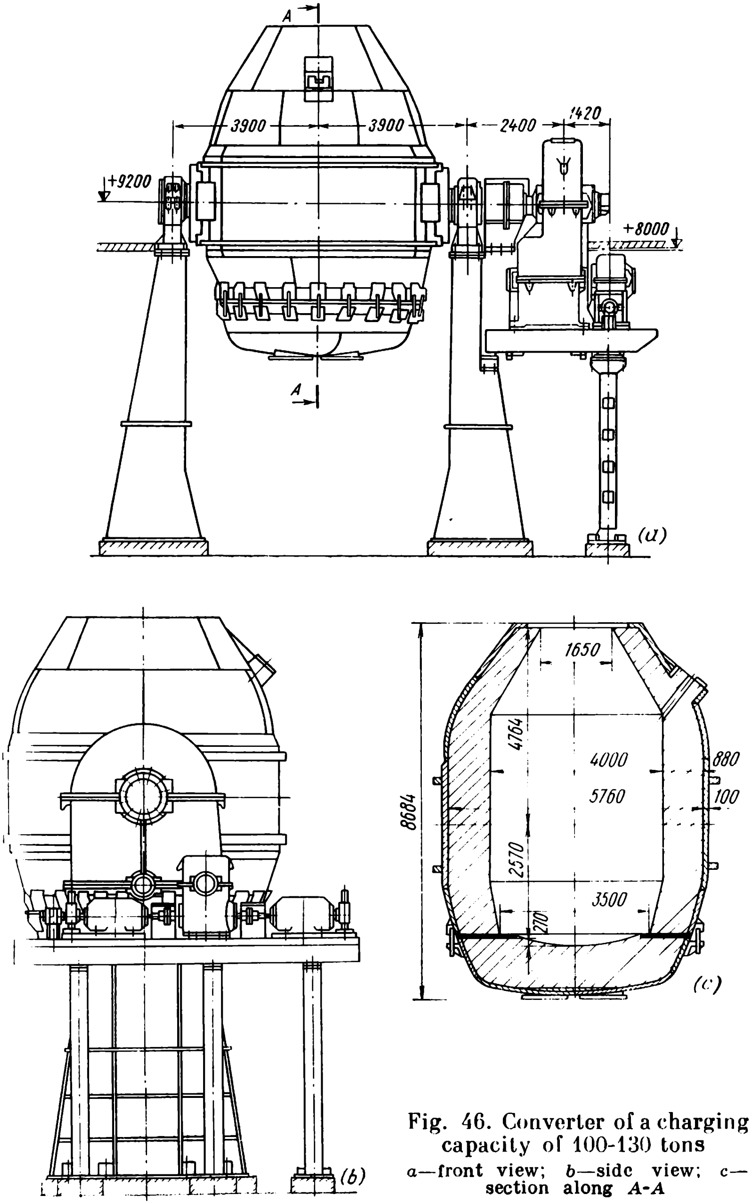

Fig. 46. Converter of a charging capacity of 100-130 tons
a—front view; *b*—side view; *c*—section along *A-A*

large capacity, the diameter of the throat is 2.5-2.8 m. The height of the throat depends on the adopted angle of tilting,

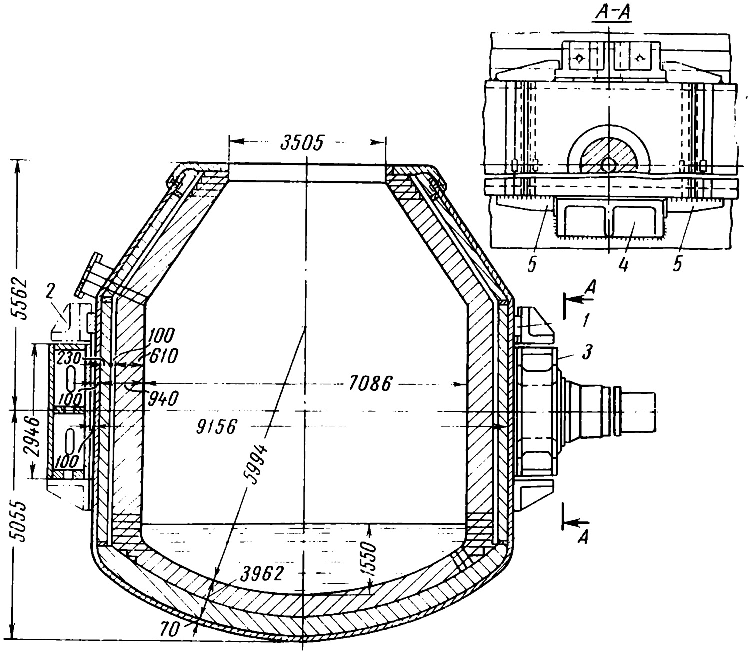

Fig. 47. 270-ton oxygen converter

1—key ring; *2*—bracket; *3*—trunnion ring; *4*—lower bracket; *5*—trunnion ring ribs

α, which is so chosen as to ensure the optimum life of the lining. For medium- and large-size converters, α varies between 53 and 71 degrees.

Figure 46 shows the vessel with a detachable bottom. Bottoms of the insert type are also in use. The bottom may be either spherical or plane. Detachable bottoms facilitate relining of vessels, since the vessel can be cooled more quickly, brick-laying is organized more conveniently with materials being supplied from below, and the whole work is done in a shorter time because the bottom may be simultaneously prepared in a separate place. The bottom is attached to the vessel by means of wedge bolts, the joint between them being sealed by applying a mixture of 20 per cent fire clay and 80 per cent periclase-spinelide powder with the addition of 3-4 per cent water glass. Converters of a capacity of more than 100 tons, however, have a solid nondetachable bottom made integral with the shell; this is done in order to make the structure more rigid and also to eliminate break-through of metal through the joint.

The conical throat portion of converters is sometimes made detachable in order to reduce repair time, since the lining of this portion is subject to rapid wear by splashed metal and high temperature, and the metallic structure is subject to buckling and cracking.

In earlier small- and medium-capacity converters, trunnion rings were cast of steel. In modern large converters, trunnion rings are of hollow welded design and fastened to the shell by means of brackets or directly by welding, or made in the form of a separate casing to which the trunnions are attached.

Figure 47 shows a 270-ton converter with a separate trunnion ring. The gap between the shell and ring is 100 mm. Attachment of the shell by means of upper and lower brackets usually does not prevent the shell against small displacements and impacts during tilting.

A trunnion ring welded directly to the shell of a 115-ton converter is shown in Fig. 48. The ring is of hollow rectangular cross-section. Air may sometimes be supplied into the ring box for cooling.

Trunnions of small-size converters bear on journal bearings, those of larger converters, on ball bearings. The bearings are mounted on cast or welded steel stands placed onto separate footings not connected with the foundations of the shop building.

The turning mechanism of a converter is a transmission gear connecting the driven trunnion with the drive motor. It can rotate the vessel through 360 degrees with a speed of from 0.01 to 2 rpm. Two-speed gear mechanisms are sometimes employed to ensure this range of speed variation. The mechanism is usually driven by two d.c. electric motors of a power of 75 to 200 kW operating simultaneously. Hydraulic drive of converters is now fully abandoned. Larger converters (200 tons and more) usually have both trunnions driven. Sometimes four motors are employed, two for each trunnion.

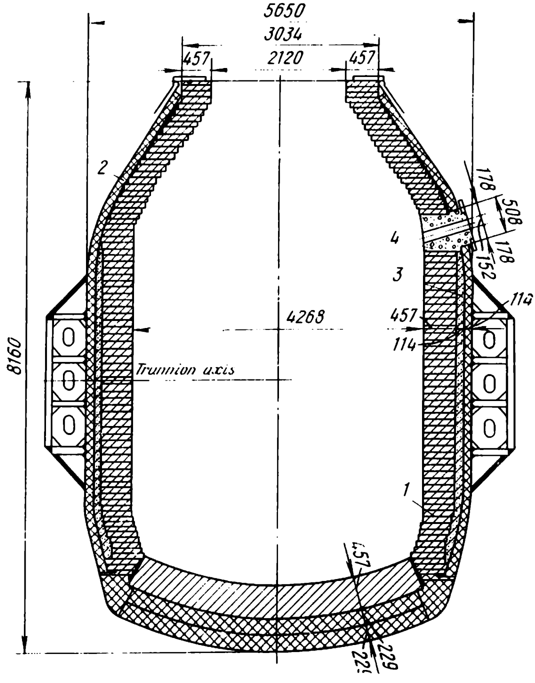

Fig. 48. Design and lining of large oxygen converter in Pueblo, USA
1—tar-dolomite brick; *2*—magnesia brick; *3*—dolomite ramming; *4*—rammed notch

The turning mechanisms usually have a certain margin of power against failure of one of the motors.

The principal design and operational characteristics of a converter for a charging capacity of 100-130 t are as follows:

Mass of charge (iron and scrap), t:	
with new lining	100
with partially worn-off lining	130-150
Working volume with new lining, m^3	80-90
Unit volume, m^3/t	0.8-0.9
Depth of liquid metal bath, mm	1500
Total height (including the bottom), mm	8684

Height without bottom, mm	7600
Maximum inner diameter, mm	4000
Height-to-maximum diameter ratio	1.9
Maximum inner diameter of shell, mm	5760
Diameter of lined throat, mm	1650
Mass (in tons) of:	
shell (without lining)	137.5
turning mechanism	102.5
stands	68.6
bearings	13.9
vessel lining	307.9
bottom lining	72.0
Distance between axes of bearings, mm	7800
Nominal rotational speed, rpm	1
Minimal rotational speed, rpm	0.1
Total gear ratio of turning mechanism	471
Blast parameters:	
oxygen flow rate, m^3 per ton of ingots	55
gauge pressure, at	12-14
Blow time, min	15-18
Tap-to-tap time, min	30-40
Annual steel output of three converters, mln t*	2.5-3.0
Load-carrying capacity of pouring and teeming cranes, t	180/50
Load-carrying capacity of cantilever cranes, t	3 and 5
Capacity of iron ladle, t	140
Volume of slag pot, m^3	16
Thickness of lining, mm:	
working layer	690
intermediate rammed layer	50
reinforcing layer	115

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* Annual output can be increased to 3.5-4.0 million tons of steel by increasing the intensity of blow to 4-5 $m^3/t \cdot min$, and therefore reducing the blow time down to 10 min.

At the West-Siberian integrated works and the Enakievsky iron and steel works, the working volume of the converters of this type has been increased against the design value to 91 m^3 and 107 m^3 respectively.

The design and operational characteristics of a 250-ton converter (which has a somewhat increased working volume and the drive via both trunnions) are given below:

Mass of charge (iron and scrap), t	250-275
Unit volume, m^3/t	1.0
Depth of liquid metal bath, mm	1500-1700
Height, mm	8490
Maximum inner diameter, mm	6500
Height-to-maximum diameter ratio	1.3
Diameter-to-bath depth ratio	4.65
Maximum inner diameter of steel shell, mm	8350
Diameter of lined throat, mm	2600
Mass (in tons) of:	
lined throat portion	200
lined vessel	567
Distance between axes of bearings, mm	12,000
Blow time, min	18-22
Tap-to-tap time, min	40-60
Load-carrying capacity of pouring and teeming cranes, t	360/100/16
Thickness of lining, mm:	
working layer (tar-dolomite brick)	620
tar-dolomite ramming	30-100
inner layer of burnt magnesite brick	100

The Lining of Converter. The life of the lining of converters depends on the resistance of its material to the eroding action of metal, slag, and dust, on its thermal shock or spalling resistance (which is characterized by the number of successive cycles of heating to 850 °C and cooling with running water until the material loses 20 per cent of its mass), refractoriness (which is the ability of the material to withstand high temperatures retaining therewith its initial shape), and its impact strength to resist heavy impacts of charged scarp. The materials commonly used for lining oxygen converters are tar-bonded unburnt dolomite and magnesite.

Magnesite is a high-refractory material which resists well the eroding action of slag, but has a low spalling resistance. Dolomite, especially when burned at a low temperature (approx. 1000 °C), is susceptible to erosion by slag and metal and to hydration.

Magnesite-chromite and chrome-magnesite bricks are also employed for lining converters. Magnesite-chromite (periclase-spinelide) brick has the following composition: 68-

71 per cent MgO, 9-15 per cent Cr_2O_3, 6-8 per cent Fe_2O_3, 1-3 per cent CaO, 4-5 per cent SiO_2, 2-4 per cent Al_2O_3, and 2-3 per cent calcination loss. Its stability is very high, mechanical strength within 490-550 kgf/cm^2, porosity 15-17 per cent and softening point 1600-1630°C. Bricks are pressed under a pressure of more than 1000 kgf/cm, and are then burnt at a temperature of 1650°C. Burning causes the formation of spinelides $MgO \cdot Cr_2O_5$ which increase the stability of the material against aggressive action of slag.

Magnesite bricks prepared under pressure from a mixture of burnt magnesite powder (grain size below 2 mm) and molasses are burnt at a temperature of 1550-1650°C. The content of MgO in magnesite bricks must be at least 91 per cent, that of SiO_2, 3-3.5 per cent, and that of CaO, not more than 3 per cent.

Dolomite brick is formed from burnt dolomite powder with the addition of tar at 560 kgf/cm^2 and burnt at 1550-1600 °C. Slag-stable burnt dolomite brick is made by pressing, drying and burning a mixture of dolomite stabilized by the additions of magnesium silicate and silica, dolomite clinker, and magnesite clinker. Bricks (45-65 per cent MgO, 22-29 per cent CaO and 10 per cent SiO_2) are characterized by a high spalling resistance and high resistance to the eroding action of slag.

Non-burnt tar-dolomite, tar-dolomite-magnesite and tar-magnesite bricks are also used to line converters. Their stability is slightly less than that of burnt bricks. The binder for non-burnt bricks is coal tar having the softening point of 80 °C and the content of pitch of 60-70 per cent. The tar serves only as a temporary binder during pressing. In operation, the volatiles evaporate and burn out, leaving a coke binder between grains of the refractory material and the carbon in grains. The carbon burns out from the lining during operation pauses between melts, when the reducing atmosphere in the vessel changes to an oxidizing one. Non-burnt refractories are subject to quicker wear owing to the loss of carbon. Bricks are pressed in hydraulic or vibrational presses at a temperature of 60-70°C. When wrapped in cellophane, bricks may be stored in air without fear of hydration for three months.

The life of non-burnt dolomite refractories in 100-ton converters reaches 500 heats. A good resistance to slag action and high spalling resistance are also shown by tar-dolomite-magnesite refractories containing 45-55 per cent MgO. The resistance to slag action increases with an increase of the density of refractories (which is the ratio of the volume of voids in the material to the total volume of brick).

The lining of oxygen converters is usually made up of three layers of brick. First, the inner layer of magnesite, magnesite-chromite or burnt dolomite brick is made, gaps between bricks and the shell being filled with tar-dolomite ramming prepared from used tar-dolomite bricks. The same ramming composition is used for making up the second, intermediate layer. The upper working layer is made of non-burnt tar-dolomite or dolomite-magnesite brick. The vessel is lined to a total thickness of 750-950 mm. The working layer determines the life of the whole lining of the vessel. The conical throat portion is lined in the same manner.

Bricks are laid dry, the joints between them being filled with powder prepared from used bricks. Expansion joints 5 mm wide are left in 1-m intervals by placing wooden spacers between bricks.

The converter bottom also has at least three layers of lining. First, a layer of fireclay or burnt magnesite brick is laid onto the metallic bottom, then a layer of magnesite brick and, finally, the working layer of tar-dolomite or dolomite-magnesite brick. The latter may sometimes be tar-dolomite rammed. The total thickness of the bottom lining is 650-1000 mm.

Topographic measurements made in a converter at the end of its campaign have shown that the lining wears off non-uniformly in various zones. This has brought forward the idea to line the vessel to different thickness in its various zones. Such a lining for a large converter is exemplified in Fig. 49. In some converters the lining thickness in the cylindrical and conical portions of the vessel is 450 mm, and in the slag belt zone and on the charging side up to 500-800 mm. The lining of the cylindrical portion of the converter in the slag belt zone and at the level of trunnions is subject to the most aggressive action of slag and high temperature of the flame. The charging side of this portion additionally undergoes wear through abrasion and impacts of scrap pieces falling down from a height of 4-8 m. The throat portion and the notch are subject to strong wear by high temperatures, dust-laiden gases, splashes, and also to damage during removal of skull. The bottom wears only under the action of slag and oxidizing atmosphere in the intervals between heats.

An effective method for increasing the life of the lining is guniting the most critical portions of the lining. Using this method, a record figure of lining life of 915 heats was attained in a 227-ton converter. The lining was laid of tar-magnesite bricks, places of the highest wear being lined with tar-impregnated magnesite brick. The lining was periodically gunited in places of the greatest wear with fine-grain magnesite-chromite mixture. The consumption of refractories was 1.59 kg, and that of guniting mass, 1.04 kg per ton steel. At some works, guniting increased the life of lining of 220-ton converters from 127 to 620 heats. During the first 100 heats, guniting was made once a day, and after 250 heats, twice a day, with layers 6-10 mm being applied. The total consumption of refractories was thus reduced from 3.5 to 2.5 kg per ton of steel, with the gunite mass used in an amount of 0.5 kg per ton of steel.

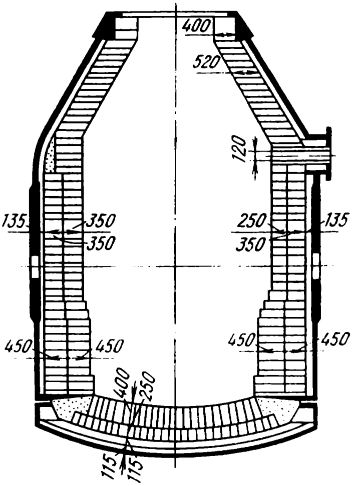

Fig. 49. Converter lining of different thickness in various zones

Another method for increasing the life of lining, which is being tested at some works, is to use non-burnt tar-dolomite blocks instead of bricks. This method appreciably reduces the number of joints in the lining, which, as is well known, serve as centres of destructive action of slag and metal on refractories. By making up a thicker lining in the cylindrical and conical portions of a converter, and by using tar-impregnated dolomite blocks placed in the slag zone and the tapping portion of the throat, the life of the converter lining was increased appreciably and its cost reduced by 60 per cent compared with the same indices for a lining made of magnesite brick. Besides, the time of relining was shortened.

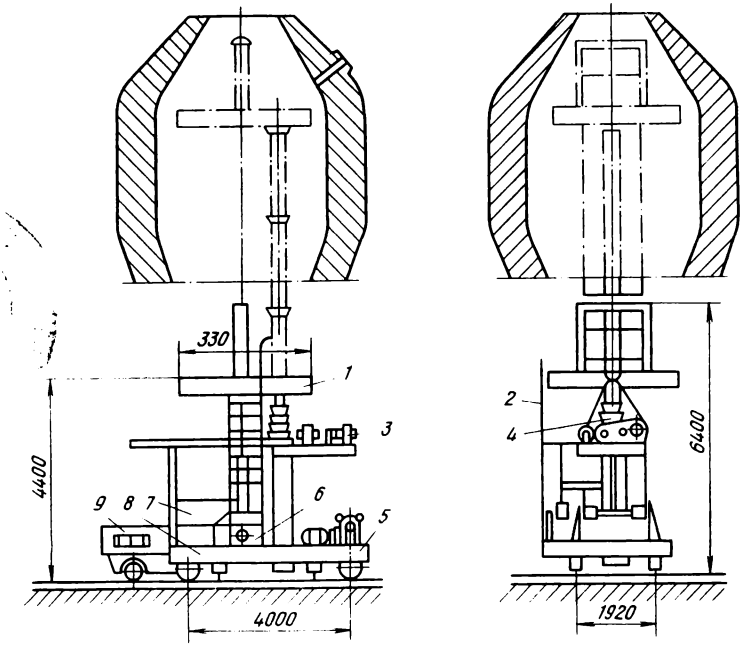

Fig. 50. Telescopic lifter for repairs of converter lining
1—working platform; 2—ladder; 3—winch motors; 4—hydraulic cylinder; 5—carriage; 6—load lifter drive; 7—load lifter; 8,9—lifters

The lining of converters is repaired in place, except for small-size converters (50-75 t) which are transferred for repair to a special repair stand by the overhead travelling crane in the converter department and replaced by the crane after repair. This repair scheme is economically inexpedient for large-size converters.

Oxygen converters are usually relined after 500-800 heats (i.e., once in 15-20 days).

The hot lining of the vessel is quickly cooled by water or air supplied by powerful ventilators. After cooling, the lining is demolished by means of various mechanical devices or pneumatic hammers. Bricks are supplied to repair places by fork trucks. The vessel is lined by using a telescopic lifter mounted on a carriage which is moved by a self-propelled teeming-ladle car. The lifter has a platform for bricklayers and a cradle for lifting bricks on bottomplates (Fig. 50).

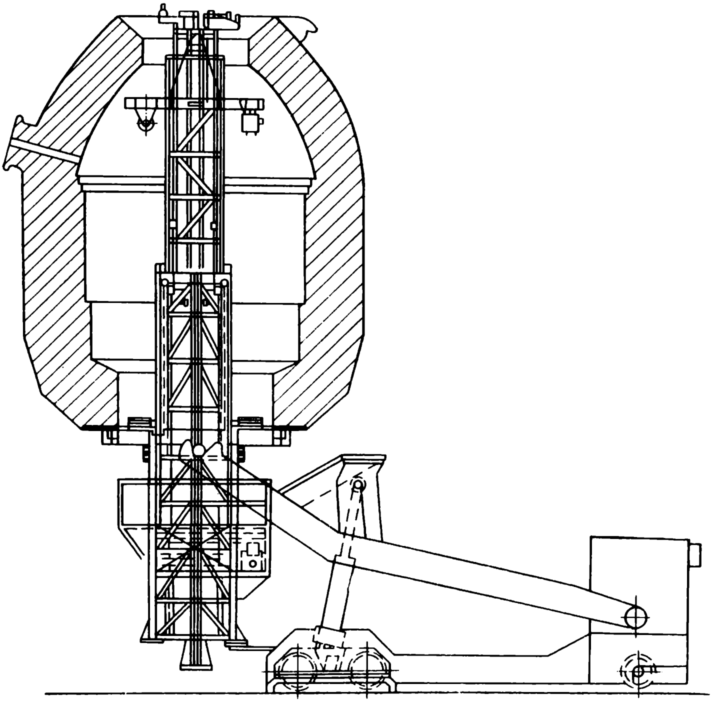

Fig. 51. Telescopic platform for repairs of converter lining

A bottomplate with bricks is placed by the fork truck onto the cradle and the latter is lifted into the vessel. Other repairing materials are supplied in the same way. Vibrochutes, belt conveyers, and pressure pipelines may also be used to supply materials. Thick pastes are carried by fork trucks in baskets of a capacity of 0.3 m^3. Detachable bottoms and throats are relined in a separate place in the shop.

A convenient telescopic platform for converter repair has been used at one of the works (Fig. 51).

Magnesite-chromite lining must be dried and heated very carefully so as to avoid spalling. Roughly 12-20 hours is required to heat it up to 1200°C. The tar-dolomite lining of oxygen converters is subjected to burning during drying. After heating the vessel must be emptied from the slag formed and only then charged with scrap.

The total time of repair of a 100-ton oxygen converter is roughly 92 hours, comprising 12 hours for chilling and demolishing the old lining, 60 hours for relining, and 20 hours for drying.

CHARGE MATERIALS FOR THE OXYGEN CONVERTER PROCESS

The charge for an oxygen converter melt is composed of pig iron, scrap, iron ore, lime, fluorspar, limestone, mill scale, etc.

Pig iron. The proportion of pig iron is 70 to 100 per cent of the metallic charge. The process is suitable for treating pig irons of any composition (acid Bessemer, basic Bessemer, or open-hearth).

High-silicon pig iron increases the amount of fluxes to be used, the bulk of slag and the loss of iron with slag, impairs the life of the lining, and complicates dephosphorization and desulphurization in the case of one-slag operation. Too low a concentration of silicon in pig iron is also inadmissible, since it may result in a protracted period of lime dissolution, i.e., a longer period of vessel operation with almost no slag; this in turn causes rapid wear of the lining at the slag belt, skulling of the lance, and poorer desulphurization of the metal.

It may be taken, as a rule, that chilling of metal with scrap allows pig iron of a higher silicon content to be used, and that the detrimental effect of the silicon will then be weakened. If chilling is to be done with iron ore, a high silicon content of the iron is inadmissible because of possible splashes and reduction in the yield of final steel.

A recommended composition of pig iron for the process is 0.7-0.8 per cent Si, 0.7-0.9 per cent Mn, not more than 0.03 per cent S, and not more than 0.2 per cent P. The temperature of the iron after pouring from the mixer into the iron ladle (measured by an immersion thermocouple) must be at least 1320 °C.

The productivity of the converter depends on the stability of pig iron composition, as well as on proper work organization in the shop.

Besides, standstills of converters between heats must be short to avoid cooling of their lining.

A factor of importance for maintaining constant composition and temperature of pig iron is proper operation of the mixer, which should be slagged off twice a day.

The pig iron supplied from blast furnaces with more than 0.8 per cent silicon may be poured into the mixer, provided that the silicon content in the mixer iron does not rise above 0.7 per cent after mixing.

An increase of the manganese content of pig iron reduces the yield of steel. The manganese concentration in pig iron is usually related to its sulphur concentration. According to some data, the degree of desulphurization of metal increases with the manganese content of iron. For that reason, the concentrations of 0.7-0.9 per cent manganese and 0.03 per cent sulphur specified for pig iron should be considered normal for one-slag operation.

One has always to consider the specific feature of the oxygen converter; process in which the rate of formation of high-basic homogeneous slag with a sufficiently high desulphurizing power is low compared with the rate of oxidation of impurities. For that reason, the effective course of the reaction of desulphurization of the metal

$$\mathrm{FeS} + \mathrm{CaO} \rightarrow \mathrm{CaS} + \mathrm{FeO}$$

can be expected to occur 1-3 minutes prior to the end of the process.

The total bulk of slag formed during the heat should be diminished by using pig iron low in phosphorus. A phosphorus concentration of 0.2-0.3 per cent requires a higher amount of lime to be used. This noticeably increases the bulk of slag, and therefore lowers the yield of steel,

Steel scrap. Steel scrap is used to chill the converter metal. The proportion of scrap in oxygen converter charges has been gradually increasing and now reaches 30 per cent of the metallic charge. Larger proportions of scrap are preferable, since scrap is cheaper than iron. With a higher temperature and higher silicon concentration of pig iron to be treated for low-carbon steel, the proportion of scrap in the charge is increased. On the contrary, treating for medium- or high-carbon steels requires less scrap to be used in the charge.

The pieces of steel scrap to be charged into the vessel must not be large to avoid possible damage to the lining. Besides, with a short intensive blow large pieces of scrap may remain unmelted by the end of the heat. The density of scrap should not be less than 2.5 t/m^3. Light-weight scrap and chips are unsuitable for the oxygen converter process as much time is required for their charging. Briquetting of light-weight scrap to a density of 2.5 t/m^3 is advisable. Waste metal from roll mills 300 × 300 mm in cross section and up to one metre long is most suitable for this process. The whole mass of the scrap may be charged from the scoop into the vessel at one go.

Iron ore. Iron ore to be charged into the converter should have at least 8-10 per cent SiO_2 with the lumps 40-50 mm in size. Dusty ore is unsuitable for charging.

Mill scale must be dry and clean and is usually charged in small amounts.

Ore agglomerate is sometimes used as coolant. It should contain not more than 8 per cent SiO_2 and not more than 5 per cent fines (below 10 mm in size) of the total amount.

Slag-forming additives. Lime and fluorspar are most often used to form slag. The most suitable slag former for oxygen-converter melting is white low-burnt lime produced by calcining in rotary furnaces at a moderate temperature, with more than 90 per cent CaO, less than 0.05 per cent S, less than 3 per cent SiO_2, and with lump size 10-25 mm, porosity at least 48-50 per cent, and a minimum amount of unburnt matter (calcination loss not more than 5 per cent). This kind of lime is especially needed with a high rate of blow, 4-5 m^3 per minute. A high porosity of lime promotes fuller reacting of ferrous oxide (owing to a greater area of reaction surface), quicker slag formation, and deeper dephosphorization and desulphurization of the metal. Dark hard lime of low porosity obtained at a high temperature of burning cannot ensure quick formation of a slag. Lime of appropriate porosity can also be produced by burning limestone in fluidized bed. Lime of a density of 1.7 g/cm^3 has a porosity of 46-48 per cent.

Lime may be replaced with limestone, but this slowers down the formation of slag, increases the blow time, makes the slag foamy, increases splashing and the amount of waste gases, and reduces the steel yield. In case of its shortage, lime can be replaced with fine-ground limestone only in an amount not more than 25 per cent of its total weight. Dolomite lime, when used instead of common lime, increases the concentration of MgO in the slag and thus prolongs the life of the lining.

50-100 kg of lime is charged per ton steel, depending on the concentrations of sulphur, phosphorus and silicon in the iron and the desired basicity of the final slag. The amount of lime for a melt can be quickly calculated by using nomograms.

Fluorspar is used to accelerate the dissolution of lime and ensure the required fluidity of slag. When converting common open-hearth pig irons, fluorspar is preferable over bauxites as containing less silicon. The quantity of fluorspar used may amount to 2-3 kg per ton of steel. The content of calcium fluoride in fluorspar must be not less than 75 per cent. Fluorspar cannot be used for treating high-phosphorus pig irons if commercial-quality phosphate slag is to be produced in the process, since it sharply reduces the solubility of slag in soil.

TOP BLOWING WITH OXYGEN IN A SOLID-BOTTOM CONVERTER (LD PROCESS)

Attempts to blow the metal with technical oxygen through the bottom of converters were unsuccessful since the refractories of tuyeres and bottom lining underwent softening under high temperatures developed in the zone of reaction of oxygen with iron impurities, saturation with iron oxide, and rapid erosion due to powerful circulation currents of the melt and blow.

Numerous experiments conducted by N. I. Mozgovoy since 1933 and also research work by Acad. I. P. Bardin have resulted in the development of the optimal version of supplying oxygen into the metal through the throat of a converter by means of a water-cooled lance. The process permits using pig irons of very diverse composition: from common open-hearth to high-phosphorus iron.

Outside the USSR, the process is commonly known as the LD process, the name derived from Linz and Donawitz, the two towns in Austria where early work on this process was carried out and the first production plants started in 1952 and 1953.

Conditions of penetration of a gas jet into a liquid were simulated on models using some liquids (water, mercury, etc.) and gases (air, steam, ammonia, etc.) which were either assimilated or not assimilated by the liquid.

As has been found, the depth of penetration of a gas jet into the melt can be described by the formula

$$h = \sqrt{\frac{\rho_g}{\rho_l g}}\, w \sqrt{d}$$

where h = depth of jet penetration, m
ρ_g and ρ_l = density of gas and liquid, respectively, kg/m^3
w = velocity of gas along the axis of the jet at the bath surface, m/s
g = acceleration due to gravity, m/s^2

As will be seen from the formula, the depth of penetration of the jet is proportional to the velocity of its motion and the square root of its diameter at the point of striking the metal.

The results of the simulation suggest the following picture of the motion of the gas jet in liquid: the gas jet first strikes the liquid and forms a cavity in its surface, the shape of the cavity being determined by the intensity of blow and the distance between the lance end and the surface of liquid. The penetrating jet partially recoils and, owing to friction, puts into motion the surrounding bath. With a low speed of the jet, the cavity is shallow, but becomes deeper as the speed of blow is increased. The liquid is atomized by the jet and, besides, splashes of metal become possible. Droplets of liquid are entrained by the outflowing gas and are carried upwards, but the main gas jet intercepts them and moves them down into the bath.

With a high pressure or at a small distance from the end of the nozzle to the bath, the oxygen jet, having the form of a torch, penetrates deep into the bath, sucks in the upper layers of liquid and disintegrates them into small streamlets and droplets, which are carried downwards by the gas jet, but as they lose their speed, droplets combine with each other and with the liquid, and the gas jet breaks into smaller jets and forms bubbles which move upwards, entraining part of the liquid in their motion.

This picture of motion and circulation of liquid and gas flows, separate jets and droplets is observed only in the upper layers of the bath. Therefore, the combined circulation motion in the bath observed on models is less intensive than the motion in the real metal-slag-gas system. One should also remember that the formula given above was derived under certain assumptions.

The actual picture in the bath of an oxygen converter is somewhat different. As has been found by studies on industrial melts, the upper layers of' the bath are essentially a slag-metal melt; motion of metal particles from metal to slag and foam proceeds uninterruptedly in the bath; the relative amount of slag in the melt is different at various levels of the foamed bath and increases from below upwards. Therefore, the nozzle is actually immersed into the slag-metal foam during almost the whole period of the heat.

By properly selecting the height of the lance above the bath and adjusting the pressure or speed of the blow, conditions may be formed at which the gas jet will penetrate still deeper into the liquid, and more intensively disintegrate it into small jets and droplets, increasing thereby the contact area between the gas and liquid.

While there is little slag in the bath, the jet of oxygen, ejected from the nozzle at a definite pressure, expands and entrains particles of the surrounding medium (Fig. 52). The gaseous products including CO that is oxidized by oxygen to CO_2 move upwards. These gases, and partially N_2, are entrained by the main oxygen jet. Therefore, O_2, CO, CO_2, and N_2 may be simultaneously present in the place where the jet strikes the metal. For that reason, the bath may be oxidized by either oxygen or carbon dioxide by the reactions:

$$^1/_2\{O_2\} + [Fe] = (FeO)$$

$$\{CO_2\} + [Fe] = (FeO) + \{CO\}$$

$$\{CO_2\} + [Mn] = (MnO) + \{CO\}$$

$$2\{CO_2\} + [Si] = (SiO_2) + 2\{CO\}$$

$$3(FeO) + ^1/_2\{O_2\} = (Fe_3O_4)$$

$$2(FeO) + \{CO_2\} = (Fe_2O_3) + \{CO\}$$

The diameter d of the jet at the place where it strikes the bath surface is larger than the initial diameter d_0, and the speed w is less than the initial speed w_0. The speed of penetration of the gas flow into metal gradually decreases owing to friction against liquid metal and the resistance of the return circulation currents. The higher the lance above the bath, the more diluted is the oxygen jet with other gases when it reaches the bath surface and the more CO afterburns to CO_2 in the converter.

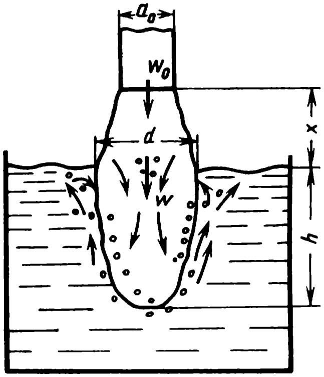

Fig. 52. Interaction of top-blown oxygen jet with liquid metal

With top blowing, as with bottom blowing, a blast zone and a circulation zone may be distinguished in the converter. In the blast zone, gaseous oxygen or carbon dioxide comes in direct contact with liquid metal or its droplets and oxidizes its impurities. Reactions of oxidation of all impurities occur at the boundaries between the gas torch and the liquid metal or metal jets and droplets, but iron is oxidized in the first place, since the rate of diffusion and mass transfer of the impurities from the bulk of the metal to its surface lag behind the rates of their oxidation. This is why a surplus of ferrous oxide accumulates in the blast zone, and thus oxygen begins to dissolve in the metal while the slag becomes saturated with ferrous oxide.

In the circulation zone, i.e., in the remaining volume of the bath, secondary reactions of oxidation of impurities occur through the action of the oxygen dissolved in the metal and of the ferrous oxide in the slag.

It is natural that the relative volumes of these zones and of the reaction zone are smaller in this case than with bottom blowing where the blow is effected through a plurality of tuyeres or holes arranged in the converter bottom. The blast zone in a top-blown oxygen converter is confined to a small volume near the surface of the bath. As has been found from simulation experiments, the depth of penetration depends on the height of the lance end above the metal, the pressure of blow, the rate of oxygen supply, and the type of lance (concentrated or expanding jet).

With the lance set low above the bath, oxygen strikes deep into metal. When the lance is 1.2 m above the bath and the blow is intensive, the energy of the jet is very high, it penetrates deep into metal and causes vigorous evolution of CO and strong mixing of the metal, i.e., forms the conditions that reduce the oxidation of the metal. The higher the lance above the bath, the greater the degree of saturation of the slag with ferrous oxide. Lifting the lance higher above the bath surface and reducing the intensity of blow cause the zone of contact of the oxygen jet with the metal to expand and the depth of oxygen penetration into the metal to decrease, thus forming the conditions at which the FeO content of the slag increases and lime is assimilated better. A temperature of 2500-2800°C develops in the zone of contact between the oxygen and liquid bath. Therefore, by varying the height of the lance above the metal, it is possible to control the distribution of oxygen between metal and slag and vary the temperature of the reaction zone. This technique was formerly very popular. In modern practice, at the beginning of blow the lance is usually set relatively high above the bath, and the distribution of oxygen between slag and metal is controlled by varying the rate of its supply while in the middle of the heat the lance is lowered as close as possible to the bath surface.

With a high setting of the lance, the processes of entrainment of CO and CO_2 into the oxygen jet, of oxidation of iron, and of afterburning of CO to CO_2 occur more intensively and a higher temperature is developed above the bath. The slag is then enriched in iron oxides, which intensifies the reactions of oxidation of impurities in the bath, i.e., the impurities that form condensed oxide phases, predominantly such as MnO, P_2O_5, and SiO_2.

The abundance of iron oxides in the slag and the high temperature promote rapid passage of lime to the slag. With such conditions of blowing, one may expect that the slag formed already at the early stage of the heat will have a sufficiently high basicity to enable the reaction of dephosphorization of the metal, which proceed simultaneously with decarbonization. Therefore, the oxygen converter process permits one to produce low-phosphorus metal without overblowing and to stop the heat at a higher carbon concentration than in the common basic Bessemer process. The oxygen converter process may even be carried out so that phosphorus will be oxidized more intensively than carbon, owing to higher concentrations of lime and iron oxides in the slag and a higher concentration of the oxygen dissolved in the metal in the zone under the lance.

The absence of nitrogen in the blast zone forms the conditions at which much excess heat is evolved in the system. The metal must then be cooled with scrap or iron ore. On the other hand, overheating of the metal in the blast zone promotes the dissolution of nitrogen that may be present in the blow. To prevent the saturation of the metal with nitrogen, the blow must contain at least 99.5 per cent oxygen.

Because of the high temperature in the blast zone, a noticeable amount of iron evaporates and is largely lost with waste gases and dust. This results in a low yield of steel relative to the metallic charge. Besides, each converter must be provided with gas-collecting devices to purify dust-laden waste gases to specified sanitary norms.

The technology of the converter heat involves the processes of oxidation of impurities and formation of slag, whose course is dependent on the composition of molten metal and the blowing and temperature conditions of the heat. To produce steel of specified carbon content and temperature, the slag and temperature conditions of the fast-run process are of prime importance as they determine the quality of steel and the technico-economical indices of its manufacture.

OXIDATION OF IMPURITIES AND SLAG CONDITIONS

Let us follow the technological scheme of the oxygen converter process taking an example of the conversion of common pig iron to steel with some scrap used in the charge. This version of the process is most advisable for the modern and future development of steelmaking in the USSR.

A solid-bottom converter is charged with the specified weight of scrap and liquid pig iron (the process is started with pouring pig iron if iron ore is to be used as coolant). Loose materials, such as lime, bauxites, fluorspar, are usually added later in the process. Upon pouring in pig iron, the vessel is turned upright, a water-cooled lance is lowered into it (a second, reserve lance must also be connected to the oxygen and water supply lines), and the metal is blown with oxygen of a 99.5-99.6 per cent purity at a pressure of 15-17 at.

Within the first minute of the blow, the first large portion of lime and iron ore (40-60 per cent of their total amount) and the total fluorspar (0.2-0.3 per cent of the metallic charge) are added to the bath via a chute. The remainder of lime and ore is charged in the converter in one or more portions in the course of the heat, most often during the 5th or 7th minute from the start of the blow.

As has been found from studies of dust formation, the dust at the initial stage of blow contains 1.8-2.5 per cent of pyrophorous iron. When the first portion of lime and other loose materials are introduced at the start of blowing, the loss of iron with dust during the first period may be 20-38 kg/min. When, however, the same amount of lime is charged 30 s after the start of the blow, the iron loss with dust becomes as high as 40-100 kg/min, since oxygen enters into the bath which is not as yet covered with slag.

Another drawback caused by the shortage of slag at the early stage of the heat is strong splashing of metal resulting in skulling of the end of the lance and its premature wear. A remedy is to add lime as soon and fast as possible. For that reason it is advisable to charge part of the specified lime over the scrap before pouring iron and to add the remainder before the intense decarbonization begins.

Oxidation of iron and silicon. The results of sampling of metal and slag in experimental melts with numerous turnings of the converter (which distort, to a certain extent, the actual picture of oxidation reactions) were used to plot the curves of the oxidation of impurities and the behaviour of slag components during the heat (Fig. 53). As will be seen, during the first few minutes of the blow iron oxidizes along with silicon, manganese, phosphorus, and carbon by the reactions

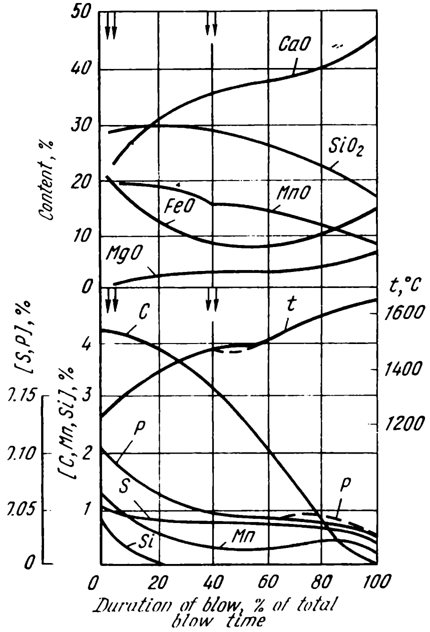

Fig. 53. Variations of metal and slag composition and temperature during the heat in an oxygen converter (the moments of adding lime and coolers are shown by arrows)

$$2[\mathrm{Fe}] + \{\mathrm{O_2}\} = 2(\mathrm{FeO})$$

$$2(\mathrm{FeO}) + 0.5\{\mathrm{O_2}\} = (\mathrm{Fe_2O_3})$$

$$4(\mathrm{FeO}) + \{\mathrm{O_2}\} = 2(\mathrm{Fe_2O_3})$$

Part of the ferrous oxide formed decomposes under the established temperature conditions and its oxygen passes into the metal solution: $(FeO) \rightarrow [O] + [Fe]$.

Silicon is oxidized more intensively than other elements:

$$[Si] + \{O_2\} = (SiO_2)$$

$$[Si] + 2[O] = (SiO_2)$$

$$[Si] + 2(FeO) = (SiO_2) + 2[Fe]$$

The silicon content of the bath becomes negligible already three to five minutes after blowing. The formation of slags rich in iron oxides begins right at blowing owing to the additions of iron-containing materials (iron ore and mill scale) as well as to the oxidation of iron.

The final reaction of fluxing of silica and the reduction of its activity in the slag promote the full oxidation of silicon in the early period of the heat:

$$2(FeO) + (SiO_2) = (FeO)_2 \cdot SiO_2$$

$$2(CaO) + (FeO)_2 \cdot SiO_2 = (CaO)_2 \cdot SiO_2 + 2(FeO)$$

Oxidation and reduction of manganese. Manganese is oxidized at the same time as silicon by the reactions

$$[Mn] + (FeO) = (MnO) + [Fe]$$

$$[Mn] + 0.5\{O_2\} = (MnO)$$

$$[Mn] + [O] = (MnO)$$

During the initial period of slag formation, when the temperature is not yet high enough to dissolve the lime completely and shells of high-melting dicalcium silicate have formed on lime lumps, MnO combines SiO_2 by the reaction

$$2(MnO) + (SiO_2) = (MnO_2) \cdot SiO_2$$

Though the temperature of the slag in the oxygen converter process is by 300 °C higher than that of the metal, with the content of Fe in the slag of less than 20 per cent, the shells of dicalcium silicate formed on the surface of lime lumps become so dense that they prevent the fluxed lump cores composed of CaO and calcium ferrites $(CaO)_2Fe_2O_3$

to pass into slag. When, however, the lance is lifted higher above the bath surface to allow the Fe content of the slag to rise over 20 per cent, the shells of dicalcium silicate are growing soft and gradually disintegrate, letting the lime dissolve completely in the metal.

With an increase of the temperature and basicity of the slag, the composition of manganese silicate changes toward substituting a stronger base for MnO by the reaction

$$(MnO)_2SiO_2 + 2(CaO) = (CaO)_2SiO_2 + 2(MnO)$$

This increases the activity of manganese oxide in the slag. The content of iron oxides in the slag diminishes by that time owing to the completion of reduction reactions of iron oxides with silicon, manganese, phosphorus, and partially with carbon.

Thus, conditions are formed for the reduction of manganese from the slag by carbon during the period of its intensive oxidation: $(MnO) + [C] = [Mn] + \{CO\}$. But in the further process, especially in melts for low-carbon steel, manganese reoxidizes in the metallic bath since the content of iron oxides in the slag increases once again. This behaviour of manganese in the oxygen-converter heat is responsible for the characteristic "manganese hump" on the melt diagram.

A higher temperature at the end of the process generally brings about a higher residual content of manganese in the steel at the same content of manganese in the pig iron. The residual manganese content in the metallic bath is made to increase by running the heat without skimming-off of the primary slag and without overblow (i.e., without substantial increase of the content of iron oxides in the slag), and also by using high-manganese pig iron. The residual manganese content of metal sometimes coincides roughly or exactly with the specification, which obviates the addition of ferromanganese for bringing the metal to the specified analysis.

Oxidation of phosphorus. Oxidation of phosphorus begins from the first minutes of blow, when the carbon content of the bath is still high. This is an essential feature of the oxygen converter process as compared with the basic Bessemer process, in which the oxidation of phosphorus begins only at the overblow period when only 0.04-0.06 per cent C is left in the bath. Phosphorus is oxidized by the following reactions:

$$2[P] + 5(FeO) = (P_2O_5) + 5[Fe]$$

$$2[P] + 2.5\{O_2\} = (P_2O_5)$$

$$2[P] + 5[O] = (P_2O_5)$$

$$3(FeO) + (P_2O_5) = (FeO)_3P_2O_5$$

$$(FeO)_3P_2O_5 + 4(CaO) = (CaO)_3P_2O_5 \cdot CaO + 3(FeO)$$

For the removal of phosphorus from metal to slag to proceed with success, the amount of free lime dissolved in the slag must be sufficiently high. By the combined reaction of dephosphorization, a rather stable compound, calcium tetraphosphate, is formed in the slag:

$$2[P] + 5(FeO) + 4(CaO) = (CaO)_3P_2O_5 \cdot CaO + 5[Fe]$$

Consequently, an active lime-ferruginous slag is required for successful dephosphorization. Let us see what changes in the slag of the oxygen converter melt must occur to ensure successful dephosphorization. As follows from the earlier discussion, the slag contains much of iron oxides already in the initial period of the heat, especially when multinozzle lances are used. As the reactions of oxidation of silicon, manganese, and phosphorus proceed (which mainly take place at the metal-slag interface), and partially as carbon is being oxidized with rising temperature (roughly during the 7th or 9th minute from the start of the blow), the content of iron oxides in the slag decreases to a minimum in the period of the maximum rate of decarbonization. The degree of oxidation of the slag again increases only at the end of the operation, i.e., at low carbon concentrations. Thus, thermodynamic conditions for the reaction of dephosphorization are ensured in the initial and in the final period of the heat, when the slag is rich in iron oxides. An appropriate basicity of the slag required for dephosphorization of the metal is established only at the end of the heat when all the lime has passed into the solution and the slag becomes homogeneous and free-running. This is natural, since, as has been shown more than once, a high content of ferrous oxide in slag speeds up the dissolution of calcium oxide. This process occurs with success in the initial and in the final period of blow, especially in melts for low-carbon steel. In the middle of the blow period, when the slag is poor in FeO, its basicity increases only slowly, since lime dissolves at a low rate. In a high-ferruginous slag, lime is assimilated quickly because the shells on the surface of lumps of CaO are composed not only of dicalcium silicate but also of calcium ferrites.

For that reason the oxygen converter process enables phosphorus to be removed from the metal without much difficulty, provided that the slag conditions have been adjusted properly. Most of the phosphorus passes from metal to slag at the very beginning of the process. The best results, as regards dephosphorization, are obtained when the final slag of the melt contains 40-45 per cent CaO, 7-14 per cent MnO, 15-18 per cent SiO_2, and 8-12 per cent FeO. But since the rate of oxidation of phosphorus lags behind the rates of oxidation of silicon, manganese, and carbon (owing to a low growth of slag basicity), the required degree of dephosphorization is usually attained by the end of the heat when the slag formed has a composition near that indicated above.

Successful and early dephosphorization of the metal is dependent to a large extent on the silicon content of pig iron. With a high silicon content, the basicity of the slag increases slowly and therefore the rate and degree of dephosphorization are not high. But the absolute initial concentration of phosphorus in pig iron has an appreciable effect, too, on dephosphorization. For instance, with the starting content of 0.15 per cent P in pig iron, the specified degree of dephosphorization (down to 0.03 per cent) is attained already at a slag basicity of 1.9-2.1. Further growth of the slag basicity up to 2.8-3.2 by the end of the heat reduces the phosphorus content to 0.01-0.02 per cent. In Japan, even lower phosphorus concentrations (0.006 per cent) in steels for deep drawing are obtained by blowing lime powder into the oxygen jet.

Experience thus shows that with pig iron containing less than 0.15 per cent phosphorus, conversion for most grades of steel may be made by one-slag operation, the slag formed in the process having a sufficiently high phosphorus-absorbing power to reduce residual phosphorus to the specification.

Desulphurization of metal. The main sources of sulphur in the metal are pig iron, lime, and mixer slag. For that reason, the contents of sulphur in lime and pig iron should not exceed the specified limits. It is also important that the slag be removed from the metal surface before pouring iron into the mixer.

As has been found, a small amount of sulphur passes from the metal into the gaseous phase under the action of blow oxygen by the reactions

$$(Fe, Mn)S + 1.5\{O_2\} = \{SO_2\} + (Fe, Mn)O$$

According to various researchers, up to 6-8 per cent of the total sulphur contained in the melt may be carried off as SO_2 with gases. But the main part of sulphur leaves metal when it passes into slag. The slag may contain such compounds as FeS, MnS, or CaS. The rate of the reaction

$$FeS + CaO \rightarrow CaS + FeO$$

is closely linked with the rate of formation of an active fluid slag and the growth of its basicity. Iron sulphide passes from metal to slag, $[FeS] \rightarrow (FeS)$, according to the distribution law $L_S = (S)/[S]$ from the very beginning of slag formation. Reactions involving the passage of sulphur into compounds which are not fully soluble in the metal also occur in the slag, their rates being dependent on the amount of lime dissolved in the slag.

Actually, it is sulphur anions that pass into slag, the process being accompanied by the simultaneous transfer of iron and manganese cations into the slag. The reactions of sulphur transfer can be written in the simplified form as follows:

$$(FeS) + (MnO) = (MnS) + (FeO)$$
$$(FeS) + (MgO) = (MgS) + (FeO)$$
$$(FeS) + (CaO) = (CaS) + (FeO)$$

The radii of Ca^{2+}, Mn^{2+} and Mg^{2+} ions are respectively 1.06, 0.91, and 0.78 Å. This difference is indicative of the fact that CaO, MnO, and MgO as slag components have different capacities for absorbing sulphur. The main desulphurizing agent among them is CaO if the lining is stable (slag contains little MgO) and if the operation is done with low-manganese pig iron.

These processes promote further transfer of sulphur from metal to slag.

Metal desulphurization proceeds slowly because it is a diffusion process. It may be speeded up by improving the bath mixing and increasing the temperature, fluidity and basicity of the slag, and the activity of sulphur.

At the initial stage of the heat, when the metal is rich in carbon and silicon, the activity of sulphur is high. Besides, part of the sulphur is removed at the initial stage of the process when the temperature of the melt is still relatively low through its reaction with manganese

$$[\mathrm{Mn}]+[\mathrm{S}]=(\mathrm{MnS})$$

A rise in the concentration of iron oxides in the slag promotes dissolution of lime, and therefore favours desulphurization.

But the secondary and most intensive desulphurization occurs at the end of the heat, when the lime dissolves in the slag with a maximum rate and the slag basicity reaches 2.8 and more. Thus the total desulphurization of the metal is mainly decided by the basicity of the homogeneous final slag which is formed in the oxygen converter process during the last minutes of metal blowing.

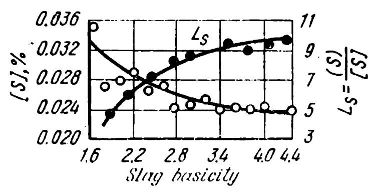

Fig. 54. Variations of the sulphur content in the metal and the coefficient of sulphur distribution depending on slag basicity

With an increase of slag basicity, the residual concentration of sulphur in the metal becomes lower (Fig. 54), so that the coefficient of sulphur distribution between slag and metal can be raised up to 10. The greater the bulk of slag is, the larger part of the sulphur will pass into slag at the same sulphur distribution coefficient. But it is not beneficial to form a very large bulk of slag, since this increases the iron loss due to burning, causes splashings and rapid wear of the lining. For that reason the total degree of desulphurization feasible in the oxygen converter process is not higher than 30-40 per cent. This should be taken into consideration when making steels with the specified sulphur content of not more than 0.015-0.020 per cent. In such cases, pig iron and lime to be used in the melt should meet more rigorous requirements as regards their content of sulphur. For instance, the practice in Japan employs additional desulphurization of pig iron tapped from blast furnaces. When the sulphur content of steel must be less than 0.015 per cent, additional desulphurization with soda is made on pouring pig iron from the mixer.

It is natural that a slag basicity of 2.8-3.0 can only be attained if a ceratin, not very high concentration of silicon is maintained in pig iron. A further increase of slag basicity does not improve desulphurization, since the slag becomes thick and therefore less active. High-basic slags can remove sulphur from metal only if they are sufficiently fluid. This is achieved by adding fluorspar or bauxites.

Alumina in bauxites accelerates dissolution of lime in slag and increases the fluidity of the latter. Fluorspar is more effective than bauxites and in addition does not reduce slag basicity, but its effect lasts only for a short time. This is possibly linked with the reaction $(CaF_2) + \{H_2O\} = (CaO) + 2\{HF\}$, following which the content of CaF_2 in the slag decreases and the latter becomes thicker. Fluorspar, when added in an amount of 0.2 per cent of the mass of the charge, ensures deeper desulphurization of metal than bauxites do, as it causes a more rapid increase in slag basicity. Besides, addition of bauxites increases the bulk of slag, since more lime must be added in order to flux their silica.

With increasing silicon content of pig iron, the degree of desulphurization lowers. On the contrary, the degree of desulphurization rises when the manganese content of pig iron is somewhat increased (within reasonable limits) so that the slag contains up to 13-15 per cent MnO. Thus, the following reaction occurs in the first period of the heat

$$(FeS) + (MnO) = (MnS) + (FeO)$$

with the subsequent exchange

$$(CaO) + (MnS) = (CaS) + (MnO)$$

With an increase of the content of ferrous oxide in the slag, the coefficient of distribution of sulphur between slag and metal usually increases, which is linked with better solubility of CaO in slag in the presence of a large amount of iron oxides rather than with the direct effect of ferrous oxide on the degree of desulphurization.

And finally, to make the metal pure from sulphur, the pig iron charged into the converter should be freed from blast-furnace and mixer slags which bring a large amount of sulphur and kish graphite into the melt. Both have an adverse effect on the course of the melt and the quality of steel.

Oxidation of carbon. Oxidation of carbon during the oxygen converter process is of exclusive importance, since the reaction increases the temperature and evolves a large amount of gases CO and CO_2 that cause agitation of metal and slag and remove hydrogen, nitrogen, and part of non-metallic inclusions from the metal. Owing to the pressure of the oxygen supplied and the evolution of large quantities of gases, the liquid bath, at least in the region of the crater (see Fig. 52), becomes an intimate mixture of slag, metal and gas bubbles, which has an enormous surface of contact. Because of this, the reaction of carbon oxidation is self-accelerated and attains a very high rate. The factors mentioned above and also the non-uniform distribution of temperature and the mechanical action of the oxygen jet, give rise to rotation of the upper layers of the bath and thereby to intensive intermixing and circulation of metal and slag. By comparing the intermixing effect of the oxygen jet on striking the metal with the lifting force of bubbles which enlarge the volume of the metal, it has been concluded that the effect of the latter is 100 times that of the oxygen jet. The oxygen jet striking the metal surface breaks the latter into streamlets and droplets which are carried by the rising currents upwards to various heights. Upon falling back into the bath, jets, droplets and pellets of metal pass through the slag and thus undergo refining and decarbonization.

It is evident that carbon oxidizes non-uniformly in the volume of the bath in the course of the operation. The highest intensity of oxidation is observed in the area of gas torch penetration. Ample evolution of gases in this volume foams up the bath, causes spouting, splashing and formation of iron beads, and thus favours decarbonization.

But at low temperatures of the process, for instance, at the beginning of the heat when the metal is still thick, the rate of carbon oxidation does not exceed 0.10-0.15 per cent per minute. At this stage the oxygen supplied is mainly used in the reactions of formation of condensed oxides SiO_2, MnO, P_2O_5, and FeO. As the reaction of carbon oxidation is slowed down in the first period of the heat, the free oxygen present in the reaction zone interacts with iron, so that the content of ferrous oxide in the slag rises to 14-16 per cent. Only after the temperature of the metal has risen up to 1440-1470°C, the rate of carbon oxidation increases to 0.4-0.5 per cent per minute. During this period, the oxidation of carbon proceeds so intensively that more oxygen is consumed than is being supplied by the jet, and carbon picks up some oxygen from the slag. The result is that the content of ferrous oxide in the slag reduces to 7-9 per cent.

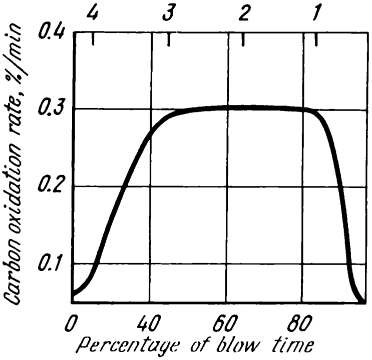

Fig. 55. Variation of the rate of oxidation of carbon during the blow of metal in a converter

A typical curve of the variation of carbon oxidation rates during the blow, with rough concentrations of carbon at certain moments of the heat, is shown in Fig. 55. As the concentration of carbon in the metal drops to 0.20 per cent, the rate of carbon oxidation decreases very sharply, and if the supply of oxygen is continued at the same rate, a large portion of oxygen is again spent to oxidize iron and the slag becomes rich in iron oxides.

One of the causes of the non-uniform oxidation of carbon during the blow is that the supply of oxygen must be reduced after the first and the second addition of loose materials in order to diminish splashing. Besides, these additions cool the metal for a short time, owing to which mass transfer of components to the reaction zone slows down. These circumstances cause a temporary reduction of the rate of carbon oxidation. But after the bath is again heated up, the rate of carbon oxidation increases sharply due to the accumulation of super-equilibrium oxygen in the metal. Vigorous oxidation of carbon after the first and second additions of loose materials and also in the middle of the heat results in foaming of the bath, so that the lance now turns out to be in an immersed position. The height of the foamed bath is usually 2-4 times the quiet bath height.

The position of the lance relative to the bath level can affect, to some extent or other, the reaction of direct oxidation of carbon

$$2[C] + \{O_2\} = 2\{CO\}$$

or the reaction of its indirect oxidation through the slag

$$(FeO) \rightarrow [O]; \quad [O] + [C] = \{CO\}$$

With an increase of the pressure and flow rate of the oxygen supplied and with the lance nozzle set nearer the bath surface, the jet of oxygen penetrates deeper into the bath and intensifies the reactions of direct oxidation of carbon. A decrease of oxygen supply and increase of the distance between the lance and the bath table result in surface reactions of oxidation of carbon through the slag.

As has been found by petrographic analysis of slag samples taken during the heat, the main constituent in the primary slag after 5 minutes of blow is manganous-ferruginous monticellite $CaO\,(Mn, Fe, Mg)O \cdot SiO_2$. Then, after the slag basicity has been increased to 1.3-1.4, dicalcium silicate $2CaO \cdot SiO_2$ and merwinite $3CaO \cdot MgO \cdot 2SiO_2$ are formed. The melting point of these free-running acid slags is roughly 1500°C. The surface of the basic lining of the vessel, being heated to a higher temperature, is saturated with this slag, loses in refractoriness, and is eroded by currents of metal and slag. A long operation with the lance set high above the bath aggravates still more the detrimental effect of the slag on the converter lining. Besides, frequent splashings destroy the throat of the vessel. With a high content of silicon in pig iron the situation may be similar or even worse.

A low silicon content of pig iron (below 0.4 per cent) may also be disadvantageous in some respects: lime is poorly assimilated, and therefore there is little slag in the bath, which causes rapid skulling of the lance end. In that case silica-containing materials (for instance, sand) are thrown over the slag. In the Japanese practice, ground silica brick in an amount of 0.1-0.2 kg per ton of metal is added, and the Acme Steel Co. (USA) use siliceous gravel.

In recent years, conditions of slag formation in large-size converters (120, 170, 220, 300, and 400 tons) have been successfully improved by using multi-nozzle lances. Former lances with cylindrical nozzles must be lifted to increase the oxidation of slag and speed up the dissolution of lime. This gave some effect, but strong splashing in the process caused rapid skulling of the throat. Apart from large losses of metal due to skulling, this reduced the output of steel, since the vessels had to be stopped every eight heats to remove skull. The application of multi-nozzle lances with the nozzles inclined 8-10 degrees relative to the lance axis improves the conditions of slag formation even at an increased intensity of blow, with the lance set rather low (1.5-1.6 m against 2.4-3.5 m for former lances). The process is run almost without splashing and provides deep dephosphorization and desulphurization. The idle time of the converter for throat repairs (removal of skull) has thus been reduced appreciably.

It follows from what has been said above that re-setting of the lance for quicker formation of slag should only be resorted to when other means (addition of fluorspar or mill scale or using nozzles of a different shape) are ineffective. Large-size converters should be operated with multi-nozzle lances set at a relatively low height above the bath. The jet formed by these lances spreads over a larger area, which increases the ratio of the reaction surface area to the bath surface area and thus ensures proper oxidation of the slag even with a high flow rate of oxygen. Such a jet prevents sintering and sticking together of lime lumps and thus favours quicker formation of slag.

TEMPERATURE CONDITIONS OF THE HEAT

As has been found from numerous experiments, exothermic reactions of oxidation of impurities in iron, especially of carbon, continuously increase the temperature of metal in the oxygen converter during the blow despite the heat loss by the vessel because of the absence of nitrogen in the blow and partial afterburning of the CO formed in the vessel to CO_2. The temperature curve becomes flat or drops only during the periods of charging of materials into the vessel. By the end of the process, the temperature of the metal increases to a high value through oxidation of iron, and it is of high importance for the quality of steel to avoid strong overheating of the metal.

The required amount of coolants (scrap, iron ore, mill scale, steam, limestone, sponge iron, etc.) is calculated from the cooling effect provided by the material at a given temperature. Steel scrap and iron ore are most often used as coolants, each of them having its own merits and drawbacks. Steel scrap provides a constant cooling effect and may be used without increasing the amount of slag formers. Besides, it causes no splashes on charging. The amount of scrap to be charged can be calculated by the formula

$$M = \frac{Q}{0.167 \cdot 1500 + 65 + 0.2\,(1600 - 1500)}$$

where M = mass of scrap, kg
Q = amount of excess heat, kcal
0.167 = heat capacity of scrap before its melting point, kcal/kg·°C
65 = latent heat of melting, kcal/kg
0.2 = heat capacity of liquid steel, kcal/kg·°C
1600 = temperature of steel, °C
1500 = melting point of scrap, °C

When scrap is used, however, additional time is required to charge it. In addition, damage to the vessel lining by heavy impacts of scrap pieces is also possible.

The use of iron ore for cooling provides certain benefits: ore may be added without stopping the blow, thus reducing the amount of oxygen to be supplied. It is assumed that one ton of iron ore containing 80 per cent Fe_2O_3, when assimilated by the bath to 90 per cent, brings in roughly 216 kg O_2, which is equivalent to 150 m^3 of oxygen. But addition of iron ore requires more lime to be added to the bath, and correspondingly increases the bulk of slag. The cooling effect of iron ore varies considerably depending on the content of iron oxides, moisture, the degree of ore reduction in the bath, and the amount of splashing and carry-off.

Limestone, lime, ore agglomerate, steam, and other materials can also be used as coolants. Their effect may be different depending on their unit heat. Some coolants can dissociate in the bath, for instance $CaCO_3 \rightarrow CaO + CO_2$; $H_2O \rightarrow H_2 + 0.5O_2$, which increases their cooling effect. An undesirable feature is the evolution of large amounts of gases. It may be roughly taken that 1 kg of iron ore is equivalent in its cooling effect to 4.4 kg of steel scrap or 0.4 kg of steam. Addition of 1 per cent of a coolant (1 kg per 100 kg of the metal in the vessel) reduces the metal temperature as follows (average data): steel scrap, by 8°C; iron ore and mill scale, 33°C; and steam, 85°C.

Coolants are chosen, however, from the conditions existing at the works and from economic considerations, rather than by the cooling effect they provide. The amount of coolants added to the melt decreases, as a rule, during the converter campaign owing to the rising loss of heat by the vessel. As has been found, heat losses of converters increase 1.5-1.6 times by the end of their campaign on account of lining wear.

The correct choice of a coolant is of high technological and economical importance. In the oxygen converter process, the waste gases carry off only 7-9 per cent of the total heat lost against 27-29 per cent in air-blown Bessemer converters. This is linked with a low concentration of nitrogen in waste gases from oxygen converters. With oxygen-enriched air blow, the gases remove 16-17 per cent of the total heat and with steam-oxygen blow, 15-16 per cent of the heat is spent for dissociation of steam. Therefore, excess heat evolves in all these processes and it is very attractive to utilize it for melting steel scrap. Increasing the percentage of scrap in the charge of the oxygen converter process is very profitable, since scrap costs less than pig iron. In the Kaldo process (discussed later in the book), excess heat is produced owing to the favourable conditions being developed for afterburning CO to CO_2 in the vessel, which makes it possible to use up to 40-45 per cent scrap in the charge.

The main coolant in the process is usually steel scrap, corrections being made by adding iron ore. Studies are being carried out into the possibilities and profits of using other coolants (ore agglomerate, briquettes, pellets, sponge iron, etc.).

BLOW CONDITIONS OF THE HEAT. DESIGN OF THE LANCE

Technical oxygen is supplied under pressure into the vessel by means of a water-cooled lance made from three seamless tubes inserted concentrically one into another. The lance ends with a nose portion which is threaded onto the inner tube and welded to the outer tube. The inner tube supplies oxygen, the intermediate cooling water, and the outer tube serves to remove heated water. The pressure and flow rate of cooling water are so chosen that the temperature of return water should be not more than 40°C. The pressure of water in the lance of a 100-ton converter is usually 6-8 at, and the flow rate, 70-90 m^3/h. The life of lances does not exceed 200 heats and depends largely on correct cooling. Failures of lances owing to burn-through by splashed metal are not infrequent.

Large converters are usually provided with two lances, one of them being in operation and the other (reserve lance) being ready for operation and connected to the oxygen and water supply lines. The setting of the lance above the bath in normal operating conditions is controlled automatically. Oxygen supply to the lance and adjustment of the lance position are remote-controlled. The operating circuit of the lance, apart from remote control means, is provided with means for automatic lifting and removal of the lance from the vessel in emergency cases: oxygen pressure loss, sharp reduction in the pressure or flow rate of cooling water. On lifting and lowering the lance, the shut-off valve of oxygen supply is respectively closed and opened automatically. The valve for controlling oxygen supply is interlocked with an oxygen flowmeter and stop-watch. The speed of motion of the lance may be controlled within 0.15-2.00 m/s.

The blow conditions have a substantial effect on the intensity of slag formation, the life of the lining and lance, intensity of splashings, blow time, and therefore on the yield of final steel and productivity of the converter. As has been indicated earlier, setting the lance at a definite height above the level of a quiet bath determines the depth of penetration of the oxygen jet into metal. The area of the surface of contact of the oxidizing gas jet ($O_2 + CO + CO_2 + N_2$) with slag and metal and the depth of penetration can be controlled by varying the setting of the lance relative to the bath surface. Therefore, the distribution of oxygen between slag and metal can be controlled in this way. The depth of penetration of the gas torch into metal is determined by the pressure and flow rate of oxygen, the height of the lance above the quiet bath, and the shape of the nozzle. The flow rate of oxygen ($m^3/t \cdot min$) and consequently the intensity of blow in the process depend on the size and mass of scrap pieces, the quality of lime, the design of the oxygen-supply line, and the throughout capacity of the gas-collecting system.

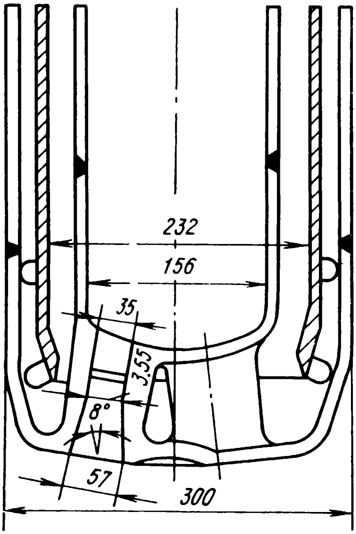

Fig. 56. Lance nose with three Laval nozzles 3 × 35 mm

The passage of the nozzle may be cylindrical, rifled, or of the Laval type. A cylindrical nozzle can eject oxygen, if its pressure is high enough, at a nearly sonic velocity. A Laval nozzle ensures supersonic velocities, which is favourable in increasing the rate of carbon oxidation and decreasing the oxidation degree of slag, foaming of the bath, and splashings.

The application of multi-nozzle lances (with three, four, or five nozzles) has made it possible to spread oxygen over a large area in the bath, which in turn has diminished the circulation of gas currents, and reduced spraying, spouting, and splashing. As has been found from comparative studies, a three-nozzle lance (Fig. 56) has the highest service life, reduces loss of metal with splashes and skull, and provides a higher yield of steel (90 per cent) and larger productivity.

With the use of multi-nozzle lances, the wider spread of the jet in the bath results in a more uniform oxidation of carbon in the course of the heat.

The advantages of multi-nozzle lances may be seen more clearly in Table 23, which gives data on their operation in large-size converters. As will be clear from the Table, almost all technico-economical indices of the oxygen converter process have been improved. In this way, it may be added that multi-nozzle lances ensure a more uniform wear of the vessel lining and reduce skulling of the throat. The use of three-nozzle lances may increase the yield of final steel by 1.0-3.5 per cent, the percentage of scrap in the charge by 2-10 per cent, and reduce the consumption of refractories by 1-2 kg/t.

Table 23

Operational Characteristics of Oxygen Converters with Multi-Nozzle Lances

Characteristics	Type of lance			
	single-nozzle, 70 mm in diameter	three-nozzle, with nozzle diameter mm		
		35	38	46
Angle of dip of nozzles, degrees	—	10	10	10
Type of nozzle	Cylindrical	Laval		
Mass of charge, t	175	200	210	210
Oxygen flow rate, m^3/min	250	310	500	600
Blow time, min	35	33	21	18
Output, t/min	5.0	6.1	10.0	11.6
Yield of steel, %	87.0	89.6	90.0	90.0
Iron loss with skull, %	1.7	0.35	0.15	0.15

Multi-nozzle lances are most often made with three or four passages of the Laval type, the axes of nozzles being set at an angle of 5-6 degrees to the lance axis (for 20-30-ton converters) or 8-15 degrees (for large-size converters). The diameter of nozzle passages in the critical section is taken equal to 30-60 mm, depending on converter capacity.

It may be concluded from Table 23 that the output of a converter may be noticeably increased by intensifying the blow, as this shortens the blow time and increases the yield of steel owing to a reduction in the metal loss with splashes and dust. The life of lining then increases too, since the time during which the lining is subject to the action of slag and metal is reduced.

It follows from the above that the main way in advancing the oxygen-converter steel process is intensification of oxygen blow from 2-2.5 $m^3/t \cdot min$ to 5 $m^3/t \cdot min$ and even more. The flow rate of oxygen in 300- to 400-ton oxygen converters planned to be built in the USSR will reach 1500-2000 m^3/min, or roughly 50 m^3 per ton of steel produced. Some metallurgists propose to raise the intensity of blow up to 7-8 $m^3/t \cdot min$ when operating with scrap. It is natural that one can intensify the blow until it impairs the conditions of scrap melting, slag formation and splashing. In that connection, a problem arises of selecting optimum blow conditions so as to melt the scrap fully during the short (10-12 minutes) blow time, ensure the best conditions for dissolution of lime and formation of slag, and distribute the large quantity of oxygen properly between metal and slag. Of prime importance here is not only the method of oxygen supply (with either one or two multi-nozzle lances), but also the number, arrangement and diameter of nozzles of multi-nozzle lances. The development of new types of lances becomes actual. In particular, lances are being developed with the central supply of water, with simultaneous supply of oxygen and various powdered oxidants, with nozzles arranged in two rows, etc.

COMBATTING SPLASHINGS

In operation of a top-blown oxygen converter, the gases carry off droplets of metal and slag. The slag-metal mixture is often splashed out from the vessel, and sometimes the slag overflows the throat. With poor blow and temperature conditions, the loss of metal may be as high as 2-4 per cent of the metallic charge.

Apart from reducing the yield of final product, splashings impair the life of the converter lining, especially of the throat, so that the vessel must be stopped for repairs in shorter intervals and its productivity thus decreases.

As has been found by experience, splashings increase in number and intensity with an increase of the depth of the bath (metal and slag) as its level rises near the throat. An increased bulk of slag in the melt is also conducive to splashings. A high setting of the lance above the bath, as we already know, causes saturation of the slag with iron oxides and more frequent splashings.

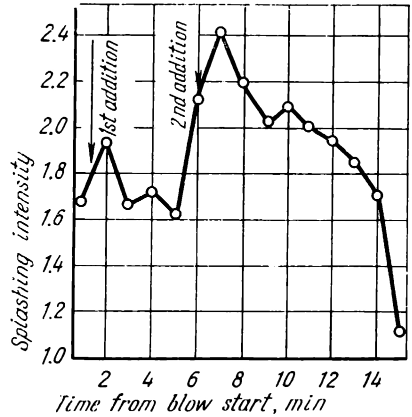

Fig. 57. Intensity of splashing in an oxygen converter with the melt cooled by iron ore

In melts cooled by iron ore, maxima of splashing are observed after the first and the second addition of ore, the second addition of ore usually causing more intense splashing. The intensity of splashing then diminishes by the end of the heat. The intensity of splashings (in conditional units) during the operation of a 28-ton oxygen converter with iron ore used as coolant is shown in Fig. 57. According to some views, strong splashings after additions of iron ore are caused by accumulation of oxygen in the chilled bath and subsequently by very intense oxidation of carbon upon reheating of the metal. As has been found by experiment, the content of iron oxides in slag after the second addition of iron ore is two or three times the usual concentration. When using iron ore as coolant, it is advisable to reduce splashings by diminishing the flow rate of oxygen by 15-30 per cent during the charging of iron ore.

In melts cooled by scrap, splashings are less strong or may even be absent.

The number and intensity of splashings depend mainly on the composition of the slag and its liability to foaming. This problem, however, has not been studied thoroughly, so that no recommendations on charging loose additives can be made here. It is only known that accumulation of iron oxides in the slag (which is possible when treating physically or chemically cold pig iron) and improper blow conditions always result in splashings. An increased content of silica in the slag causes foaming of the latter, and therefore may promote splashings during the intense oxidation of carbon. On the contrary, a high content of dissolved CaO in the slag reduces foaming and thus causes less splashing.

As has been observed, no splashing occurs at the moment of charging additives, since the rate of carbon oxidation reduces at that moment. This means that chilling of a foamed slag-metal mixture causes the foam to sink. A method sometimes practised is to lift the lance high above the foamy bath to strike the foam with the oxygen jet. Splashings of foamed slag may be prevented by throwing fine river gravel or small portions of limestone.

One may recommend the following most effective measures to be taken to diminish or eliminate splashes: (a) reduce the flow rate of oxygen for a certain time as soon as splashings begin or somewhat earlier judging by the intensity of noise in the vessel; (b) divide the specified amount of loose additives into more portions to be given to the bath to ensure more uniform evolution of gases and reduce pulsations of the bath; (c) keep the bath level in the vessel as low as possible, mainly by reducing the bulk of slag; (d) use various fluxes in order to dissolve the lime in the slag as soon as possible, so that the critical basicity of the slag (1.5-1.7) can be attained before the reaction of carbon oxidation begins to proceed most intensively; (e) use spreaded jet so as to minimize sticking of lime lumps; (f) reduce foam-

Table 24

Material Balance of an Oxygen Converter Melt (prior to deoxidation) per 100 kg of Metallic Charge

Input, kg		Output, kg	
Liquid pig iron	85.000	Steel	90.012
Steel scrap	15.000	Slag	13.419
Bauxites	0.600	Iron beads in slag	1.000
Lime	5.870	Gases	9.168
Technical oxygen	7.767	Dust losses	2.638
Lining wear	2.000		
Total	116.237	Total:	116.237

Table 25

Heat Balance of an Oxygen Converter Melt (prior to deoxidation) per 100 kg of Metallic Charge

Input, kcal (%)		Output, kcal (%)	
Physical heat of pig iron	24,300 (49.70)	Enthalpy of:	
Heat from oxidation of C, Si, Mn, P, and Fe	23,356 (47.84)	steel	31,252 (64.60)
Heat of slag formation	1 206 (2.46)	slag	7 192 (14.70)
		waste gases[1]	3 763 (7.70)
		Heat carried off by splashed Fe_2O_3 particles	1 020 (2.10)
		Radiant and convective heat losses	1 759 (3.60)
		Excess heat	3 876 (7.90)
Total:	48,862 (100.00)	Total:	48,862 (100.00)

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[1] Of these on heating gas constituents, kcal (%): CO and CO_2, 3484 (7.15); N_2, 13 (0.02); H_2O and SO_2, 122 (0.24); O_2, 144 (0.29).

ing of the slag by controlling the content of silicon in the charge and lowering the quantity of oxygen supplied to the slag; and (g) use multi-nozzle lances instead of single-nozzle cylindrical lances.

The existing practice of supplying oxygen at a constant rate during the whole blow time is, without doubt, inconsistent and should be changed. To do this, however, more rational redistribution of oxygen during the periods of the heat should be proved by experience. This is the work for the near future.

We conclude our discussion on the top-blown solid-bottom oxygen converter process by presenting Tables 24 and 25 that give the material and heat balances of the melt.

TREATING VANADIUM PIG IRON IN OXYGEN CONVERTERS

As has been indicated, the use of oxygen-blown converters has changed many processes of steelmaking. This, in particular, relates to conversion of vanadium pig iron.

At the Nizhne-Tagilsky integrated works, mixer iron (4.2-4.9 per cent C, 0.2-0.3 per cent Si, 0.2-0.25 per cent Mn, 0.15-0.20 per cent Ti, 0.38-0.49 per cent V, 0.05-0.11 per cent P, 0.025-0.06 per cent S, and 0.1-0.5 per cent Cr) is treated in 100-ton oxygen converters to produce carbon semiproduct and vanadium-containing slag. The process used is as follows: 110-112 tons of pig iron (at a temperature of 1250°C) is poured from the mixer into the vessel, with roughly 5 per cent mill scale and 6 per cent vanadium-rich scrap or solid pig iron being added as coolant. Oxygen (99 per cent pure) is supplied at a pressure of 11-14 at and at a flow rate up to 230 m^3/min by a water-cooled three-nozzle lance. The latter is set 0.7-1.2 m above the level of the quiet bath.

The blow time is 7-10 min and tapping is at a temperature of 1340-1400°C. The semiproduct made has the following analysis: 3.2-4.0 per cent C, 0.03-0.04 per cent V, 0.05-0.08 per cent P, and 0.015-0.04 per cent S.

Figure 58 shows variations in the metal and slag compositions in two melts, one of them being cooled with solid iron and mill scale, and the other with scale only.

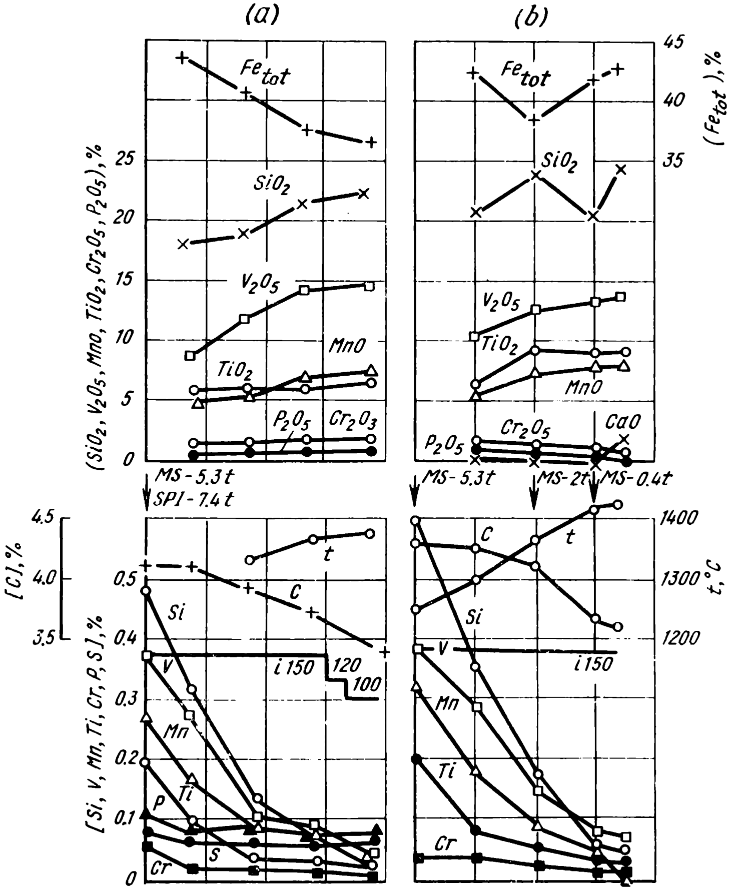

Fig. 58. Variations of the composition of metal and slag in a top-blown oxygen converter when treating vanadium pig iron for semi-product

a—cooling with solid pig iron (SPI) and mill scale (MS); *b*—cooling with mill scale (MS) only

The semiproduct is tapped from the vessel into the ladle and transferred to an open-hearth furnace (i.e., a duplex process: converter—open-hearth furnace is performed) or poured into another oxygen converter for refining and making steel of the specified composition (i.e., a duplex process: converter—converter is made). The second version is now practised on industrial scale. The vanadium slag is used for making ferro-vanadium.

The vanadium slag from melts for semiproduct is very viscous at the temperature of tapping (1340-1400°C) because of the presence of spinelides. Its composition is: 17-23 per cent V_2O_5, 15-20 per cent SiO_2, 6-8 per cent TiO_2, 5-8 per cent MnO, 34-41 per cent Fe (total), 1-3 per cent MgO, 1-2 per cent Cr_2O_3, 0.04-0.07 per cent P, 0.03-0.09 per cent S, 0.40-0.90 per cent Al_2O_3, and 0.5-1.5 per cent CaO. The yield of semiproduct is 96 per cent and fluxing of vanadium pig iron in the process is 93 per cent. The consumption of oxygen is 16 m^3 per ton of pig iron.

After running-off the vanadium slag, the semiproduct is tapped into the ladle and then poured into another oxygen converter, all operations being made in 10-15 minutes with special measures taken to minimize heat losses (the temperature of semiproduct thus decreases only by 30-40°C). In the second converter, the semiproduct is treated for mild steel. The metal is blown with oxygen (99.5 per cent pure) supplied by a water-cooled three-nozzle lance at a flow rate of 200-280 m^3/min. Lime, fluorspar, and iron ore or iron flux (34-44 per cent CaO, 5.0-7.0 per cent SiO_2, and 33-41 per cent total Fe) are charged at the beginning of blow. The blow time is 18-22 minutes, the end of the melt being decided by the amount of oxygen spent.

Since there is almost no manganese in the semiproduct, it is advisable to replace iron ore with manganese ore; this will favour partial reduction of manganese and require less ferro-manganese to be added for deoxidation of steel.

The final slag contains 35-45 per cent CaO, 2-3 per cent MnO, 18-20 per cent total Fe, 9-11 per cent MgO, and 4-6 per cent SiO_2. The yield of final steel is 87-89 per cent of the metallic charge of the first converter. The consumption of oxygen is 40 m^3/t in the second converter and 50-55 m^3/t for the whole process.

Chapter Nine

TREATING HIGH-PHOSPHORUS PIG IRONS IN OXYGEN CONVERTERS

When treating pig irons of common phosphorus content (0.1-0.3 per cent P) in oxygen converters, removal of this element encounters no difficulties, even in operation without slagging-off. The situation is different with high-phosphorus pig irons (1.8-2.0 per cent P), the main difficulty being in that much lime must be added to the melt to remove the phosphorus. With a 'mild' blow, conditions can be formed to induce lime lumps to stick together and form large pieces. Since fluorspar cannot be used for making the slag more fluid (it sharply reduces the solubility of phosphate slags in soil), the process becomes very complicated and must be run with two slags.

When treating high-phosphorus pig iron, the commercial phosphate slag obtained should have the content of P_2O_5 as high as possible.

The problem is that the rate of oxidation of phosphorus in the process adopted must be equal to or somewhat higher than the rate of carbon oxidation from the very beginning of the heat. Then the process may be carried out without overblow. If the concentration of phosphorus in the melt is not lowered sufficiently by the end of the melt when the carbon concentration has dropped to the specified value, further blowing of the metal to oxidize the remaining phosphorus will be protracted and result in a lower yield because of high loss of iron during the overblow period.

Let us discuss some processes of treating high-phosphorus pig iron in oxygen converters.

These processes are aimed to ensure higher rates of phosphorus oxidation than they are in the process of conversion of low-phosphorus pig irons. As is known, the steeper is the rise in the oxidizing potential and basicity of the slag and the quicker is the increase in the temperature of the metal and slag, the greater is the rate of phosphorus oxidation; in other words, conditions for a rapid formation of iron oxides in the slag are required to be set in to speed up the dissolution of lime and thus increase the slag basicity. The common LD process is unable to provide these conditions to full extent, for all loose materials are added in lump form, and the slag cannot be formed sufficiently quickly.

THE OLP, OCP AND LD-AC PROCESSES

The OLP (oxygen-lime powder) process was developed at the Institute des Recherches Sidérurgiques (IRSID) in France for conversion of high-phosphorus pig iron containing 1.8-2.0 per cent P, 0.2-0.6 per cent Si, 0.3-0.8 per cent Mn, and 0.02-0.08 per cent S by blowing it with oxygen and powdered lime. In its industrial application, the process uses mainly iron ore as coolant. The OLP process ensures quick formation of slag and deep dephosphorization. The total lime required for the melt is introduced with the blow. Pig irons with not more than 0.3 per cent Si and 0.6 per cent Mn are most suitable for the process.

A similar process was developed at the works in Dudelange (Luxembourg) by the ARBED concern and the Centre National des Recherches Metallurgiques of Belgium and Luxembourg (CNRM). It was initially named the OCP process, by the initial letters of the French words "oxygene chaux pulverice" (oxygen-powdered lime). The two processes were later combined under the general name the LD-AC process, where A stands for ARBED and C, for CNRM.

The LD-AC process is essentially as follows. One-third of the total lime specified for the melt is charged in lumps 40-60 mm in size into the vessel prior to pouring pig iron, the remaining lime being blown in powdered form together with oxygen through a water-cooled lance 3-5 minutes after the start of the operation. The grain size of lime powder is from a few hundredths of a millimetre to two millimetres. The fine lime powder used has a very large surface area of contact with oxygen and metal. It is heated up and melted quickly and passes into the slag melt at an early stage of the operation, with the result that the reaction of dephosphorization of the metal develops at the same time as, or somewhat earlier than, the reaction of carbon oxidation. The coolant (iron ore) is added in small portions from the very beginning of the heat, which forms initial conditions for the reactions of dephosphorization

$$2[P] + 5(FeO) \rightarrow (P_2O_5) + 5[Fe]$$

and

$$3(FeO) + (P_2O_5) = (FeO)_3P_2O_5$$

with subsequent retention of phosphorus oxides in the slag upon dissolution of the lime by the reaction

$$(FeO)_3P_2O_5 + 4(CaO) = (CaO)_3P_2O_5 \cdot CaO + 3(FeO)$$

If scrap is used as coolant, it is charged into the vessel in the proportion of 10-15 per cent of the metallic charge together with some lime and bauxite prior to pouring in pig iron. The blow is started at a high setting of the lance, powdered lime being blown in together with oxygen. Slag formation is controlled by varying the setting of the lance above the bath or by varying the pressure of oxygen blow with the lance fixed.

In 60- to 75-ton converters the first period of the blow continues for 12-14 minutes, after which the blow is stopped and roughly 90 per cent of the slag is skimmed off, its composition usually being 20-22 per cent P_2O_5, 48-54 per cent CaO, 7-9 per cent SiO_2, and 8-10 per cent FeO. The metal at that moment contains 0.13-0.20 per cent P and 0.8-1.2 per cent C. After slagging-off, scrap is charged into the vessel (or iron ore is added periodically) and the blow with oxygen and lime powder is re-started, and continues by the end of the heat, this taking 3 to 5 minutes. Thus, the total blow time is 17-20 minutes. The total amount of lime is 80-120 kg per ton of steel, of which 60-80 kg are used in the first blow period and 30-40 kg in the second. The percentage of scrap is 18-25 of the metallic charge, the flow rate of oxygen is 55-57 m^3 per ton of pig iron or somewhat lower if iron ore is used instead of scrap to cool the melt. The yield of slag is 150-170 kg per ton of steel.

In Luxembourg, this process is used for making mild and medium-hard steels. A two-slag operation is run when making steels for deep drawing, and also steels of a medium (0.2 per cent) and high (0.5-0.6 per cent) carbon content. In these cases desulphurization and dephosphorization are deeper than in the one-slag operation, the final values being

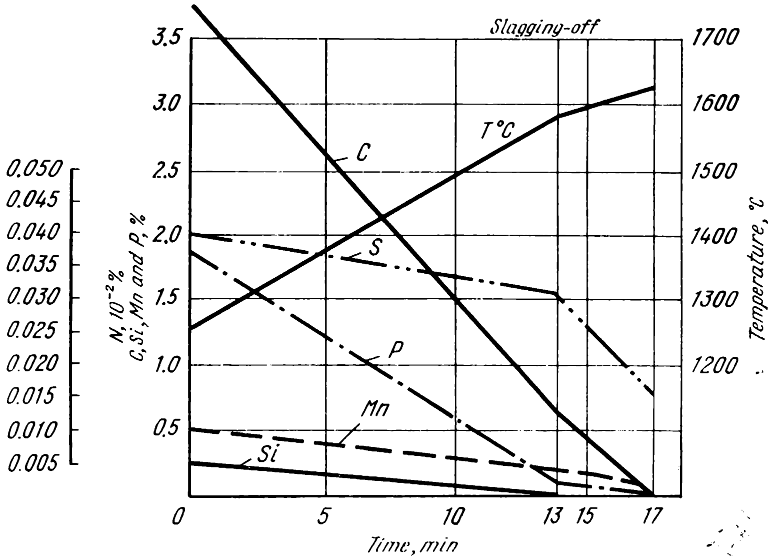

Fig. 59. Variations of metal composition during blowing with oxygen and lime powder (the LD-AC process)

0.016-0.017 per cent P, 0.015-0.016 per cent S, and 0.002-0.003 per cent N when 99.5-% pure oxygen is used. The tap-to-tap time in the two-slag operation usually increases somewhat owing to turning down the vessel for carbon sampling and subsequent overblowing.

In Western Europe, the LD-AC process is used for treating high-phosphorus pig irons. When making medium-carbon steels, it is possible to stop the blow at a desired carbon concentration, since the rate of oxidation of phosphorus in the process is always higher than that of carbon.

Figure 59 shows variations in the composition of the melt blown with oxygen and powdered lime. The principal diagram of a plant for effecting the LD-AC process is illustrated in Fig. 60.

After tapping, the final slag is left in the vessel for the next heat, which makes it possible to use less lime and oxygen, but the cycle lasts 3 minutes longer because pig iron must be poured slowly onto the slag in the vessel.

The process was tried out in the Federal Republic of Germany for treating common pig iron with 0.18 per cent P and proved of small advantage in dephosphorization over the common LD process with the use of lump lime (10-30 mm in size). According to modern views, the supply of powdered lime to the oxygen blow is reasonable only when treating high-phosphorus pig irons. Metallurgists are at work on further improvement of the LD-AC process. Methods are being searched for to attain better desulphurization and dephosphorization, in particular, by using two lances or forming a large bulk of final slag so as to reduce the content of P_2O_5 in it to 4.0-4.5 per cent. With a high basicity of such a slag, the metal under it can be refined to 0.01 per cent P and 0.015 per cent S.

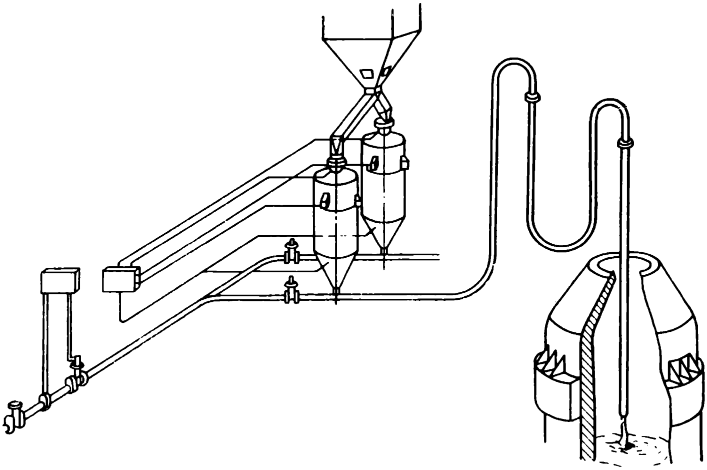

Fig. 60. Diagram of converter plant for the OLP (LD-AC) process

The oxygen-converter shop in Chertal is the largest in Belgium. It produces steel by the LD-AC process. Let us discuss certain essential features of the operation of the shop. Since it has no blast furnaces, pig iron for the converters is transported from the works in Seraing, 22 km away, in mixer ladles of a capacity of 350 tons. The rate of temperature drop in the mixer ladle is 4-5°C per hour. The maximum time for keeping pig iron in mixer ladles provided with refractory-lined covers is 60 hours. The ladle is carried by a 32-wheel flat car, the load per wheel being 10 tons. This makes it possible to transport pig iron in mixer ladles along common railway lines with a speed at least 40 km/h, i.e., to distances up to 200-300 km.

The mixer ladle is lined with fireclay brick containing 42 per cent Al_2O_3. A hot repair by guniting is made after the first 300 fillings, after which the ladle serves for another 200-300 fillings. Guniting is repeated three or four times during the ladle campaign. It is planned to increase the ladle campaign up to 2800 fillings by using high-alumina brick (67 per cent Al_2O_3) and making up to eight hot repairs.

Oxygen (99.6 per cent pure) for the converters in Chertal is supplied at a pressure of 30 at from Seraing via 300-mm pipelines. The pig iron treated in converters contains 3.9 per cent C, 0.6 per cent Mn, 1.9 per cent P, 0.4 per cent Si, and 0.04 per cent S. If the content of S is more than 0.04 per cent, or the steel must have only 0.015-0.020 per cent S, pig iron is additionally desulphurized with soda during pouring it into intermediate iron ladles. The sulphurous slag is skimmed off from iron ladles by a special machine. Soda is used in an amount of 500-1000 kg per 125 tons of pig iron, which ensures desulphurization by 60 per cent.

The heat is started with the deoxidation of the final slag left in the vessel from the previous heat by adding granulated pig iron (5 t) and coke (650 kg), after which the vessel is charged with 125 tons of liquid iron and, without any interval, 30 tons of scrap. The first blow period takes 15-18 minutes with oxygen being supplied at a rate of 400 m^3/min by a three-nozzle lance. A few minutes after the start of the blow, powdered lime is supplied in an amount of 3.6 t for the first period.

The first blow period is stopped when the metal contains 0.5-0.6 per cent C and 0.1-0.2 per cent P, after which the initial phosphate slag (containing roughly 18-22 per cent P_2O_5, 50 per cent CaO, and 8-11 per cent of total Fe) is skimmed off. Upon adding 14 tons of steel scrap, the bath is overblown with oxygen (at a rate of 500 m^3/min) and powdered lime during 5-8 minutes. The final steel contains 0.05-0.08 per cent C, 0.01-0.02 per cent P, 0.02 per cent S, and 0.002 per cent N. The final slag (48 per cent CaO, 6-8 per cent P_2O_5, and 25 per cent of total Fe) is left in the vessel for the next heat. The tap-to-tap cycle is 50-55 minutes and the consumption of oxygen, 57-60 m^3 per ton of steel. The life of the lance is 150 heats, since the wear of its nozzle by powdered lime is not high. The temperature of the metal is controlled by adding mill scale or small-size scrap, silicocalcium being used when a need arises to increase the temperature. The yield of steel is 87.3 per cent.

Specialists of the works in Chertal hold that when converting high-phosphorus pig irons, the productivity of the vessel reduces by 20 per cent and the yield of steel, by 0.8 per cent as compared with the same indices for the conversion of common open-hearth pig irons.

THE LDP (POMPE) PROCESS

The process employed in Pompe (France) and Rheinhausen (FRG) for treating high-phosphorus pig irons is based on using graded lump lime. The heat is carried out with two blow periods, and therefore with two slags, the final slag being left in the vessel for the next heat. The vessel is provided with a special notch for better separation of metal from slag in tapping. The process is suitable for making mild and medium-hard steels, i.e., the blow may be stopped at a specified carbon content.

Let us follow the blow and slag conditions in the process during making rimming steel in 20-ton converters. Variations of the contents of impurities and the moments of additions of lime and iron ore during the heat are shown in Fig. 61.

During the first blow period, the metal becomes deeply dephosphorized long before the carbon content of the bath decreases appreciably. The vessel with the slag left from the previous heat is first charged with some lime (lumps not more than 40 mm in size), after which pig iron (1200-1250°C) is poured in slowly, for 4-5 minutes. The blow is started with the lance set low above the bath and at a high pressure of the oxygen supplied. The temperature of the bath rises

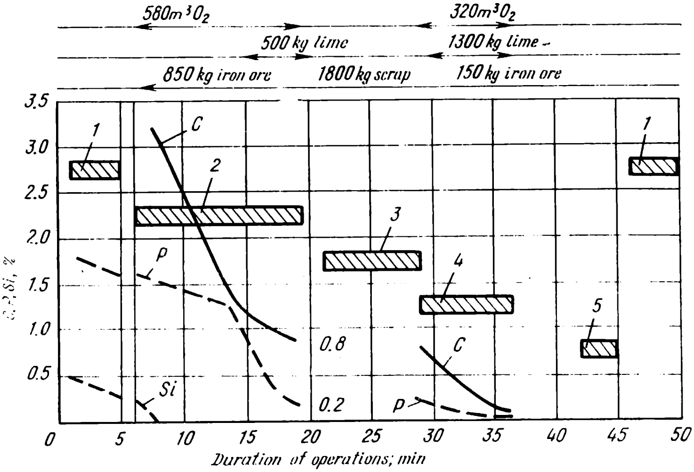

Fig. 61. Graph of a melt for rimming steel in an oxygen converter (Pompe Works)

1—pouring-in of 18 tons of pig iron; 2—first blow; 3—skimming of slag and charging of 1.8 tons of scrap; 4—second blow; 5—tapping

quickly and is controlled by continuously adding iron ore via a chute. After 10 minutes of blowing, the lance is set higher in order to increase the content of FeO in the slag and thus speed up the dissolution of lime. From that moment on, graded lime is fed to the bath via the chute. The high temperature of the bath and ample amount of FeO in the slag cause quick dissolution of the lime, so that oxidation of phosphorus attains a high rate already at the 12th minute of the blow. The lance is then lowered into its initial position and lime is added via the chute (500 kg specified for the second blow period). After the oxygen specified for the first period (580 m³) has been spent and the temperature of the metal has reached 1550-1650°C, the blow is discontinued and the initial slag (composed mainly of 23 per cent P_2O_5, 10 per cent FeO, and 50 per cent CaO) is skimmed off. As can be seen from Fig. 61, the metal at that moment contains 0.8 per cent C and 0.2 per cent P.

The second blow period is started with charging 10-15 per cent of the specified scrap and forming new slag by adding 1300 kg lime and 150 kg iron ore to the vessel. The blow is done with the lance set high and oxygen (320 m^3 specified for the second blow) fed at high pressure. The contents of FeO and CaO in the slag then rise rapidly and ensure a deep dephosphorization of the metal. Foaming of the slag is controlled by lowering the lance, which at the same time reduces the content of ferrous oxide in the slag. The heat is finished when less than 0.1 per cent C remains in the metal. The final slag left in the vessel for the next heat contains 10 per cent P_2O_5, 30 per cent FeO, and 50 per cent CaO. The total amount of the initial slag can then be used as commercial by-product, which reduces the consumption of oxygen and cost of steel by 4 per cent. The total usage of oxygen reaches 50 m^3 per ton of steel. Leaving the final slag in the vessel increases somewhat the time for pouring iron, since the latter must be poured carefully to avoid splashing. But this is compensated for by the rapid formation of slag, so that the tap-to-tap cycle shortens. The process is employed at the Pompe works with success for making both killed steel (45 per cent) and rimming steel (55 per cent). The life of the vessel lining is 100-110 heats i.e., much lower than in the LD-AC process. The melt is usually cooled by using both scrap and iron ore (iron ore being used in the first period, and scrap and a small amount of ore in the second). If scrap alone is used as coolant, its consumption reaches 30 per cent and the usage of oxygen increases to 60-64 m^3 per ton of steel.

THE PHOENIX-LANZEN PROCESS

A combined process for treating high-phosphorus pig irons was developed at the Phoenix-Rheinrohr works in Ruhrort (FRG). It essentially consists in blowing the metal with air (or oxygen-enriched air) through ceramic tuyeres arranged in the bottom of the converter and technical oxygen blown to the surface of the bath via a water-cooled lance.

The blow in the vessel is carried out in three stages (Fig. 62). At the first stage, air or oxygen-enriched air (35-40 per cent O_2) is blown through the bottom of the vessel, while scrap, iron ore or ore pellets containing up to 98 per cent Fe_2O_3 are being added to the metal. The lime (8-15 per cent) that has been charged prior to iron pouring dissolves quickly in the slag owing to these additions of iron-containing materials and to intensive mixing of metal and slag. This promotes oxidation of carbon and phosphorus. The temperature of the metal during this period is not very high and does not induce the nitrogen of the blast to pass to the metal. By the end of this period, 50 per cent of the phosphorus oxidizes and roughly 0.3 per cent carbon remains in the melt.

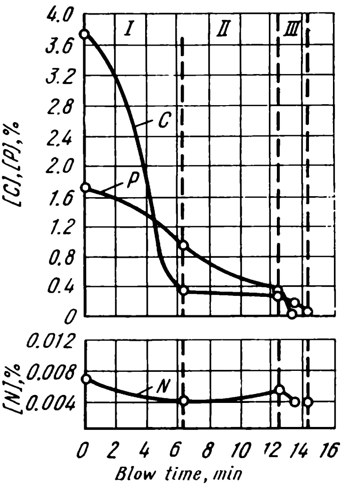

Fig. 62. Variations of metal composition in the Phoenix-Lanzen process

I, *III*—bottom blowing of the vessel; *II*—top blowing with oxygen

At the second stage, the vessel is turned down (Fig. 63) and the lance is introduced through the throat to supply technical oxygen at a high pressure onto the slag. Because of the rise of temperature and afterburning of CO to CO_2 in the vessel, ferruginous-lime slags form rapidly and the phosphorus of the metal intensively oxidizes down to 0.2-0.3 per cent P. The blow is then discontinued and the vessel again turned upright to start the third stage, which essentially is overblowing by means of air (or oxygen-enriched air) supplied through the bottom tuyeres. This stage takes only one or two minutes, this time being sufficient to oxidize phosphorus down to a few hundredths of a per cent, since the high-basic slag formed in the bath now mixes well with the metal.

The final steel contains 0.03-0.10 per cent C, 0.02-0.04 per cent P, and 0.018-0.022 per cent S. By skimming-off the initial phosphate slag and forming a new slag, which is usually done at the end of the second stage in melts for high-carbon steel, the metal can be dephosphorized and desulphurized to a deeper extent. For instance, in experimental heats of basic Bessemer pig irons steels of good quality were produced with the contents of elements (in various grades) as follows: 0.05-0.21 per cent C, 0.28-0.52 per cent Mn, 0.025-0.032 per cent P, 0.009-0.024 per cent S, and 0.003-0.005 per cent N. As can be seen, by using technical oxygen at the second stage of the process and oxygen-enriched air at the first and third stages, it is possible to convert basic Bessemer pig irons into steels having the nitrogen content not more than in common open-hearth steels.

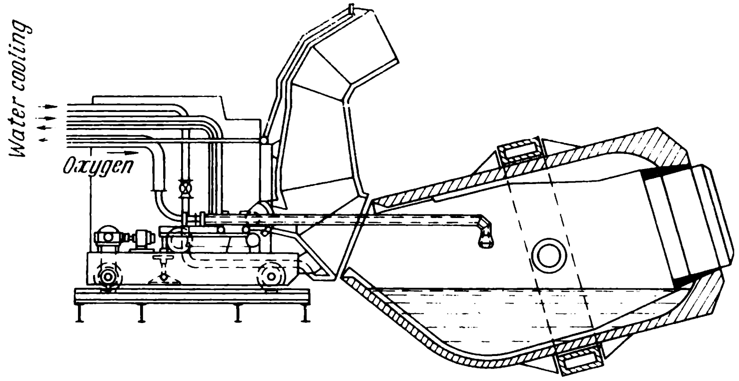

Fig. 63. Oxygen blowing of basic Bessemer pig iron by means of a water-cooled lance in the Phoenix-Lanzen process

The total tap-to-tap time was 15 minutes and the oxygen consumption, roughly 70 m^3 per ton of steel, including the oxygen for enriching air. Thus, the process consumes little oxygen and therefore does not require large oxygen-producing plants. The phosphate slag produced is of commercial quality.

The Phoenix-Lanzen process is rather complicated because of the need to turn the vessel up and down several times during the operation and thus can be recommended only for small scale production in existing converter shops.

THE BUFFER SLAG PROCESS

The process was developed at the works in Hagen-Haspe (FRG) and essentially consists in that high-phosphorus pig iron is top-blown in the vessel with oxygen in such a manner that oxygen does not contact directly the metal most of the period of the heat, but is picked up by the slag. The impurities in the bath are oxidized through further passage of the oxygen via the slag-metal interface to the metal, i.e., similar to what occurs in an open-hearth furnace. Common open-hearth pig irons can also be treated by the process.

The heat begins with pouring pig iron into the vessel and then charging one-third of the specified amount of lime and iron ore. The metal is then blown during a few minutes with a low setting of the lance and a high pressure of the blast in order to quickly heat up the bath and form free-running slag, following which the lance is set to the upper position and the blast pressure is reduced. From that moment on, the remainder of the lime and iron ore is continuously added into the vessel in small portions, and the blow conditions are controlled so as to avoid contact between the oxygen jet and metal. The blowing through the thick layer of slag is stopped for running-off phosphate slag (or continued to the end of the operation if no slagging-off is specified). The slag produced is of commercial quality owing to a high content of phosphorus; phosphorus is oxidized in the process with the same rate as carbon. After slagging-off, lime and iron ore are loaded to form a new slag and also a specified amount of scrap is charged into the vessel. The overblow is carried out with the lance set in the lower position in order to reduce the content of iron oxides in the slag.

The purity of oxygen has but an insignificant effect on the content of nitrogen in the metal, since there is no direct contact between the metal and the blow in the process. By using technical oxygen of a purity of 95-96 per cent, steels of low nitrogen content can be produced.

Another advantage when passing oxygen to the metal through the slag buffer is the prevention of local overheating of the metal in the reaction zone beneath the torch and reduction in the formation of iron-oxide dust, which is characteristic of the ordinary LD process. The process is therefore run almost without formation of brown fumes, provided that the slag cover is sufficiently thick. But foaming of slag and splashings are not infrequent in the process, which are to be taken account of when selecting the unit volume of the vessel. The quality of steels produced is equivalent to open-hearth steels. Economic merits of the process are not yet clearly defined.

THE KALDO PROCESS

The Kaldo process, developed by Prof. B. Kalling at the Domnarvet works in Sweden, is essentially oxygen blowing in a rotating converter. The vessel, which is of the solid-bottom type lined with tar-dolomite brick (outer layer) and magnesite brick (inner layer), can be turned through 360 degrees around its transverse axis and rotated around the longitudinal axis with a speed of up to 30 rpm (Fig. 64). Blowing is done with the vessel set at an angle of 17-20 degrees to the horizontal by means of a water-cooled lance (or two lances) inclined at an angle of 26 degrees to the surface of the bath. Oxygen is supplied at a pressure of 3-4 at.

The lance may be additionally tilted by 7-10 degrees from the initial position and oscillated in order to spread the oxygen jet wider over the bath. Oscillations of the lance and rotation of the vessel prevent local overheating of the metal in the zone of oxygen supply (which is characteristic of LD converters).

This technique and the "soft" invariable blow result in a shallow penetration of the oxygen jet into the bath, which lessens the formation of brown fumes and the dust loss of iron and thus increases the yield of steel. The volume of waste gases from the Kaldo converter is less by a factor of 6 to 8 than that in the LD process. For that reason the gas-cleaning plant may be of simpler design.

Since the vessel is turned low during the operation, the bath is covered, as it were, by a roof, so that up to 90 per cent of the CO evolved burns to CO_2 inside the converter. This changes radically the heat balance of the melt, namely offers a twofold increase in the heat from oxidation of impurities in the metal as compared with that evolved in the LD process (where this heat is approximately one-third of the total heat supplied). For that reason the Kaldo process can use up to 45-48 per cent scrap in the charge, which is of special importance in view of the general trend toward increasing the production of steel from pig iron and scrap in oxygen converters and gradually decreasing the production of open-hearth steel. Because of the large proportion of scrap in the charge, Kaldo converters may be recommended for works having the excess of cheap scrap and deficiency in liquid iron. The coolants in the process are iron ore, sponge iron, solid pig iron, etc.

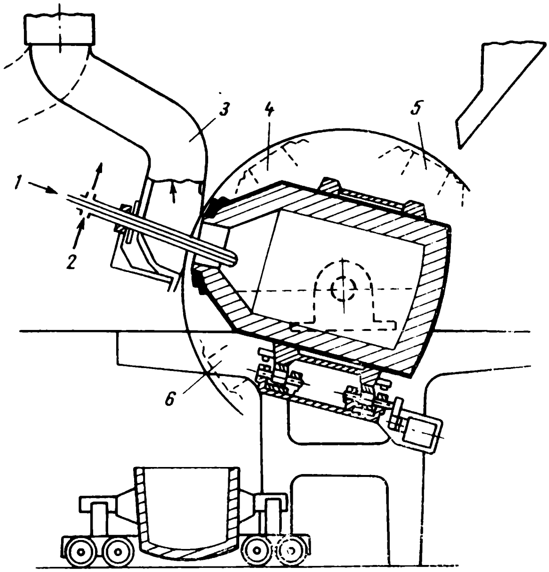

Fig. 64. A Kaldo converter

1—oxygen supply; 2—supply and removal of water; 3—removal of waste gases; 4—position of the vessel for pouring-in pig iron; 5—position for charging lime and iron ore; 6—tapping position

The Kaldo process is suitable for treating both low-phosphorus (common conversion) and high-phosphorus (basic

Bessemer) irons, but is mainly used for treating high-phosphorus grades, since the favourable thermal conditions of the process (owing to afterburning of CO to CO_2 and better contact between metal and slag in the rotating vessel) ensure quick dissolution of lime and formation of active lime-ferruginous slags and therefore oxidation of phosphorus and sulphur at an early stage of the heat. It will be noted that rotation of the vessel makes it possible to supply oxygen at a lower pressure than in the LD process.

The thermal, slag, and blasting conditions of the Kaldo process can be easily controlled by varying the flow rate and pressure of the oxygen supplied and the rotational speed of the vessel.

The easy control of the heat, the favourable thermal conditions enabling a large proportion of scrap (or iron ore) to be used in the charge, a low loss of iron, and therefore a high yield of final steel (up to 93 per cent) make the Kaldo process very advantageous.

Since there is no splashing in the course of the heat, the unit volume of Kaldo vessels can be taken as low as 0.50-0.65 m^3 per ton of steel.

The fumehood turns the waste gases leaving the vessel through an angle of 90 degrees, which causes coagulation of dust particles to a size of 3-20 μm. This largely facilitates gas cleaning. The amount of dust in waste gases is 17-20 g/m^3. The gases are cooled in a water-cooled chimney down to 1000°C and then in spray chambers, to 150°C. The cooled gas is cleaned from dust in electric settlers and electric filters to a purity of 99.5 per cent.

The principal drawbacks of the Kaldo process are a longer blow time (40 minutes for high-phosphorus iron and 30 minutes for common pig iron) than in the ordinary LD process; longer tap-to-tap time; complicated driving mechanism; and a short life of the vessel lining owing to vessel vibration in rotation, high temperature in the working space (as a result of almost complete burning of CO to CO_2), and continuous eroding action of slag and mechanical friction of metal. Despite the fact that the vessel lining is cooled somewhat by the metal during rotation, droplets of metal stick to it, are oxidized by the blast oxygen, and the iron oxides thus formed destroy the softened surface layer of the lining.

The last drawback can be lessened by increasing the content of carbon in the working layer of the lining (i.e., by using more tar binder). The excess carbon diminishes the infiltration of iron oxides, partially reduces them and in general slows down their penetration into the depth of the lining. For instance, the wear of the cylindrical portion of Kaldo converters has been reduced to 7 mm per heat by using tar-impregnated burnt magnesite in the outer layer and even less (to 3 mm per heat), by using molten-cast refractories.

The Kaldo process is employed at present for making very diverse grades of steel: very soft rimming steel to make sheets intended for deep drawing (0.07-0.08 per cent C, 0.25-0.38 per cent Mn, 0.013-0.015 per cent P, 0.012-0.018 per cent S, and 0.002-0.0035 per cent N), soft killed steels,

Table 26

Selected Data on Operation of Kaldo Converters

Parameters	Works		
	Domnarvet	Seremange	Charon
Capacity, t	30	131	140
Average carbon in final steel, %	0.08	0.05	0.25
Charge, kg/t steel:			
liquid iron	1016	670	650
scrap	—	405	430
iron ore	170	20*	8*
lime	135	87	40
Maximum usage of O_2, m^3/min	40	220	340
Unit usage of O_2, m^3/t steel	60	62	58
Fe oxidized in slag, kg/t steel	32	25	13
Loss of Fe, kg/t steel	24	23	36
Blow time, min	40	41	38
Tap-to-tap, time, min	72	80	—
Output, t/h	25	110	—
Yield of final steel, %	91.0	90.5	90.75

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* Pellets.

medium-hard, and high-carbon steels. Some works produce chrome-alloyed quality steel by the Kaldo process. Apart from low concentrations of phosphorus, sulphur and nitrogen, Kaldo steels are known to be low in hydrogen (0.00025 or even 0.00015 per cent).

Table 26 gives some operational characteristics of Kaldo converters.

THE ROTOR PROCESS

The diagram of a cylindrical rotor furnace is shown in Fig. 65. The vessel is mounted horizontally and rotates during the heat around its longitudinal axis with a speed of 0.1-4.0 rpm. The length of the furnace of a capacity of 60-145 tons is roughly 15 m, and the outside diameter, 3.7-4.6 m. Openings of a diameter of 0.6-1.25 m are provided at both ends of the vessel to charge materials, supply oxygen, and remove slag, metal and gases. Slag is tapped through an end opening by tilting the vessel. A special slag notch is sometimes provided for the purpose.

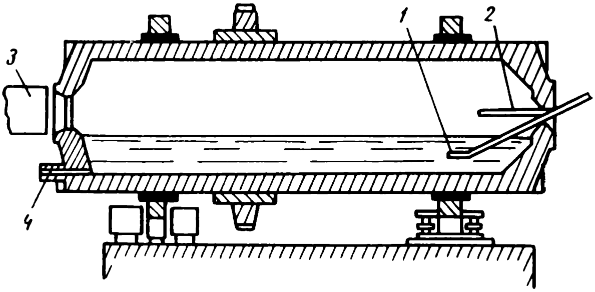


Fig. 65. A rotor furnace

1—primary oxygen; 2—secondary oxygen; 3—waste gas outlet; 4—tapping hole

The vessel is fastened in a cradle mounted on a horizontal rotatable platform. This arrangement allows one to rotate the vessel about its longitudinal axis, turn it through 360 degrees in the horizontal plane by any one of its ends, and turn through 180 degrees in the vertical plane.

The vessel is lined with an inner layer of magnesite brick and an outer layer of tar-dolomite (or magnesite) brick, over which a layer of tarred dolomite is rammed. Two carriages with lances for separate delivery of oxygen into the bath and the working space are mounted at one end of the rotor furnace and a fumehood for removing waste gases, at the other.

Rotor furnaces are mainly used for treating high-phosphorus pig iron. The scheme of the operation is as follows.

Iron ore and lime are charged into the furnace onto the slag left from the previous heat by means of a charging machine of the throwing type. The tapping hole is then plugged and hot metal poured into the vessel. Blowing with oxygen is started with the simultaneous rotation of the furnace.

Oxygen is supplied through two water-cooled lances. One of them is immersed to a depth of 250 mm into the bath and supplies the primary oxygen of a purity of 90-99 per cent at 6 at to oxidize impurities in the iron and improve mixing of metal and slag. The second lance serves to supply the secondary blast (oxygen-enriched air at a pressure of 3 at in which the content of oxygen is varied between 30 and 70 per cent) into the working space above the slag; this is used to burn the CO evolved from the bath to CO_2 and thus to increase the utilization of heat in the furnace. In modern practice, powdered iron ore (grain size up to 2 mm) and lime are sometimes added to the secondary blow to speed up slag formation. The ratio between the primary and secondary oxygen was formerly 1 to 4. For example, 15-20 m^3 of primary oxygen and 60-65 m^3 of secondary oxygen were used to make one ton of steel from high-phosphorus pig iron.

When converting high-phosphorus iron into final steel, the blow is continued until 0.1-0.2 per cent phosphorus (and roughly 2 per cent carbon) remains in the bath, after which the furnace is stopped and the initial slag skimmed off. Lime and iron ore are then added to form a new slag and the blow is re-started, with the furnace being rotated, to lower the phosphorus and carbon contents to the specification. When tapping the metal, most of the secondary slag is left in the vessel for quicker formation of slag in the next heat and for better utilization of phosphorus oxides.

The primary slag contains 18-20 per cent P_2O_5 and can be used as fertilizer. The blow time for making final steel is about 60 minutes, and the total tap-to-tap time, including charging, iron pouring, slagging-off, and sampling, is roughly 120 minutes.

When the furnace is used to make a semiproduct for its subsequent conversion in an open-hearth or other unit, the blow time is 30-40 minutes, and the tap-to-tap time, 60 minutes. The process is stopped at 1.5-1.8 per cent C and 0.1-0.2 per cent P in the metal. Common low-phosphorus pig iron is always treated for final steel; the tap-to-tap time is then shorter and the consumption of lime is smaller.

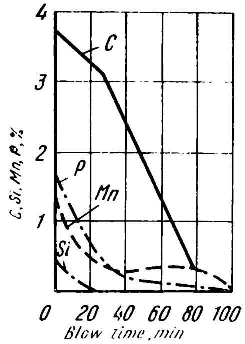


Fig. 66. Variations of the composition of the metal (high-phosphorus pig iron) during melting in a rotor furnace

Figure 66 shows variations in the metal composition in a rotor furnace when treating high-phosphorus pig iron for steel. As will be seen, silicon oxidizes completely already at an early stage of the heat. The concentration of phosphorus drops to 0.1-0.15 per cent by the moment when the metal still contains roughly 2 per cent C. The behaviour of manganese in the course of the heat and its noticeable residual concentration in the melt determine the high-temperature process in the rotor furnace. This behaviour of impurities in the rotor furnace makes the rotor process suitable for producing quality and high-quality steels containing 0.03-0.6 per cent C, 0.012-0.020 per cent S (with 0.05-0.06 per cent S in the iron), 0.002-0.004 per cent N, and 0.015 per cent P (in rimming steels) or 0.022 per cent P (in killed medium-carbon steels). As has been established from the analysis of the material balance of the rotor heat and from the samples of waste gases, sulphur is partially removed as gaseous SO_2 (up to 15 per cent of its total amount). The total degree of desulphurization reaches 65 per cent for irons of common sulphur content (0.05 per cent) and may be even higher with a higher initial sulphur concentration in pig iron.

Owing to the specific design of the rotor furnace and the supply of secondary oxygen into the space above the slag, the CO evolved from the bath is almost fully burned to CO_2, the additional heat from this reaction being roughly equal to the total amount of heat from oxidation of the elements in the charge. This makes it possible to operate the rotor furnace with up to 60 per cent scrap in the charge or to use an equivalent amount of iron ore.

Modern practice gradually abandons the method of full afterburning of CO to CO_2 in the rotor furnace and some plants restrict to a minimum the supply of secondary oxygen. The allowable content of CO in combustion products is now 30 per cent, against 6 per cent allowed in the former practice, that is, the secondary blast is now done with air rather then with oxygen. This solution is attributed to the need of reducing the unit consumption of oxygen, diminishing the unnecessary excess heat evolved in the furnace (which is detrimental to the life of the lining), and also to the possibility of utilizing the waste gases as fuel.

Though the primary oxygen is introduced directly into the bath of the rotor furnace, the overheating of the metal in the reaction zone and the evaporation of iron are not so strong as in the ordinary LD process, since masses of the metal in the reaction zone are continuously intercharged owing to the rotation of the vessel. Dust particles carried off with gases have enough time to settle partially and coalesce on their way to the chimney, since the furnace is rather long. The gases are further cooled down to 250°C on passing through a cyclone separator and disintegrator, cleaning them from dust to 96 per cent. The dust collected in the form of sludge is used in the furnace, instead of ore concentrate or mill scale.

The rotor process has not found wide application. The existing rotor furnaces in Great Britain and the Republic of South Africa are used for treating high-phosphorus and open-hearth pig irons.

The life of the lining of 145-ton rotor furnaces (Republic of South Africa) is reported to last for 500 heats, but other data give rather lower values. The usage of oxygen is 42 m^3 per ton of steel (including 35 m^3 of primary oxygen). The output of rotor furnaces is 80 t/h and the yield of ingots is 87.5 per cent (disregarding the usage of ferroalloys).

As has been found by tests, steels produced in rotor furnaces are comparable in their properties to open-hearth grades and, in particular, are suitable for electric welding.

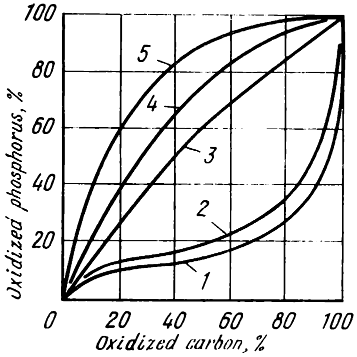


Fig. 67. Rates of oxidation of carbon and phosphorus in high-phosphorus pig iron treated by various converter processes

1—bottom blowing with atmospheric air; *2*—bottom blowing with oxygen-enriched air; *3*—LD process; *4*—LD-AC and OLP processes; *5*—blowing in a rotor furnace

The curves in Fig. 67 show variations of the rates of oxidation of carbon and phosphorus in high-phosphorus pig irons treated by the various converter processes with various kinds of blasting. The marked difference, especially between the two extreme curves, may be explained by different conditions for the formation of active lime-feruginous slags.

In the basic Bessemer process where the metal is blown through the bottom of the vessel with air (curve *1*) or even with oxygen-enriched air (curve *2*), the rate of oxidation of phosphorus noticeably lags behind that of carbon oxidation, which is linked with a late formation of the slag. The ability of the slag to pick up phosphorus increases rapidly only in the overblow period after lime has been dissolved. But only about 2 per cent of the initial carbon remains in the metal by that moment. The causes for slowering down the kinetics of phosphorus oxidation in these processes have been discussed earlier. The principal cause is too low a temperature for melting films of $(CaO)_2 \cdot SiO_2$ enveloping lime lumps, and therefore a late passage of lime into the slag solution, and also an insufficient amount of oxygen in the bath for the initial oxidation of phosphorus owing to a high activity of interaction between the carbon and the oxygen dissolved in the metal.

In the LD process (curve *3*), the rates of oxidation of carbon and phosphorus are almost the same owing to a rapid growth of temperature of the metal and slag in close proximity to the oxygen torch penetrating the bath. This is attributed to the intermixing between the metal and slag and to an earlier passage of lime into the slag.

In the LD-AC process (curve *4*), where high-phosphorus pig iron is blown with oxygen with the addition of powdered or graded lime, the surface of contact between the metal and slag increases sharply from the very beginning of the process, which forms favourable thermodynamic and kinetic conditions for oxidation of phosphorus and gradual acceleration of this reaction as the basicity of the slag is being increased.

Finally, in the rotor process (curve *5*) the conditions are the same as in the LD-AC process (curve *4*), but rotation of the vessel provides better mixing of metal and slag, which improves diffusion and convective processes and therefore accelerates the formation of a slag possessing a high activity to phosphorus, so that the rate of oxidation of phosphorus becomes much greater than that for carbon. For that reason the LD-AC process and rotor process can be used for making medium- and high-carbon steels without overblow or subsequent carbonization of the metal in the ladle.

The choice of some or other process for conversion of high-phosphorus pig irons should be done on the basis of thorough technico-economical analysis.

Chapter Ten

MELT CONTROL, QUALITY OF STEEL, AND TECHNICO-ECONOMICAL INDICES OF OXYGEN-CONVERTER PROCESS

CONTROL OF THE MELT

The short period of the converter heat requires quick monitoring of the temperature and carbon concentration in the metal to decide on the correct moment for turning down the vessel and ensure the required steel temperature on tapping, a fact which is of high importance for making steel of the specified quality.

There are a number of methods for controlling the converter heat. In the Bessemer process, photo-cells are employed to measure the brightness of the flame. A photo-electric device continuously records the brightness characteristic of the flame. The record made by the instrument shows directly the variations of carbon concentration in the metal, since the radiance of the flame depends on the content of carbon oxide in the gases, i.e., on the rate of carbon oxidation. The blowing of the metal is stopped when, according to the indications of the instrument, the carbon content drops down to the specified limit.

The moment for turning down the vessel at a specified carbon content (for instance, 0.6 or 0.7 per cent) may be determined quite accurately by a differential method using two photo-electric cells. The essence of the method is in measuring the difference between the intensities of radiation in two places, or the ratio of the photo-currents produced by two photo-electric cells. The intensity of radiation varies in different way in various regions of the spectrum, and the difference may be clearly sensed by two photo-cells. The results obtained by this method are then corrected by chemical analysis of a sample of the metal taken from the vessel after its turning down.

The contents of carbon and silicon in the sample can be quickly determined by the method developed at the Enakievsky iron and steel works, which essentially consists in measuring the thermo-e.m.f. induced in a circuit containing a hardened sample of the metal series-connected thereto. For this, a sample of the metal is taken from the vessel and poured onto a shovel. After solidification, a thin cake forms which is immediately hardened in cold water, ground by an emery disc, and placed between two copper contacts of a measuring device. One of the contacts is cold and the other is automatically heated to have a constant temperature difference (150 to 200°C) between the hot and the cold joint. The thermo-e.m.f. is measured by a calibrated galvanometer. It has been established that at carbon concentrations in the metal within the range of 0.1-1.0 per cent, the magnitude of thermo-e.m.f. is strictly proportional to the carbon concentration in the sample, provided that the silicon concentration is not more than 0.05 per cent. At higher concentrations of silicon, a correction is found by using another, not hardened, sample of the same metal. The whole operation for determining carbon and silicon by the method takes only two minutes.

Another method for determining the moment of turning down the vessel in the oxygen converter process is by the flow rate of oxygen consumed in the heat. The usage of oxygen for the heat is preliminarily determined under standard conditions. In operation, after the specified amount of oxygen has been consumed, the oxygen flow-rate integrator gives a signal for turning down the vessel, which also causes automatic stoppage of the blow and lifting of the lance.

At some works metal temperature is controlled directly by means of an optical pyrometer fitted in a water-cooled pipe which is inserted through the throat of the vessel and directed onto the surface of the bath. Measurements are continued for 15 seconds, after which the pipe is withdrawn from the vessel. Readings of the pyrometer are recorded by an automatic recorder and used for controlling the temperature conditions of the heat. The method is sometimes used for continuous measurement of temperature, the pyrometer being protected from the hot metal by blowing in argon or nitrogen. A small amount of nitrogen used for the purpose has no effect on nitrogen content of the metal in the vessel. Methods of direct temperature measurement now in use employ immersion thermocouples of the Pt-Pt/Rh, W-Mo or W-Re type which are immersed into the metal on turning down the vessel. In certain cases metal temperature is measured continuously by sheathed Pt-Pt/Rh termocouples. A thermocouple, protected by a refractory sheath, is placed in the converter lining at a height near the level of the quiet bath, flush with or protruding a few millimetres above, the surface of the lining.

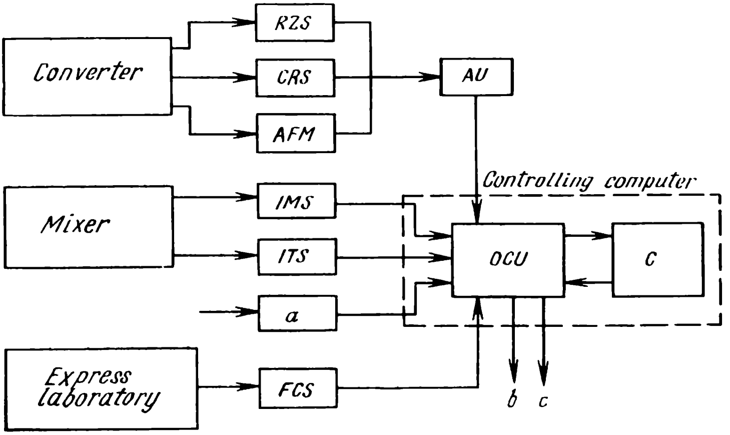


Fig. 68. Principal diagram of automatic control of a Bessemer converter with the use of an УМШН controlling computer

OCU—object communication unit; *C*—computer; *IMS*—iron mass sensor; *ITS*—iron temperature sensor; *FCS*—sensor of carbon content in final steel; *a*—manual input of data on chemical composition of iron; *b*—signal for turning down the converter; c—data for controlling the consumption of iron ore; *AU*—amplifier unit; *RZS*—reaction zone sensor; *CRS*—sensor of radiation in converter; *AFM*—air flowmeter

Schemes also exist in which the moment for stopping the blow is determined by the content of CO and CO_2 in converter gases. The moment for turning down the vessel is found on the basis of the data pertaining to the amount of carbon burnt during the various stages of the blow period and the total amount of CO and CO_2 evolved from the bath.

A "liquidus" method is coming in use for simultaneous determination of metal temperature and carbon concentration by throwing sampling "bombs" into the throat of the vessel.

In the recent time, mathematical models of the process are being developed with the aim of forming mathematical programs (algorithms) for computer control of converter operation.

Figure 68 shows the principal circuit for computer control of Bessemer converter operation based on the use of a universal controlling computer type УМШН developed at the Institute of Cybernetics of the Ukrainian Academy of Sciences. The machine is supplied with the data obtained from two radiation sensors, a blast flowmeter, a tensometric sensor of the amount of pig iron, and a thermo-electric instrument measuring the content of carbon in a sample of final metal. The data on temperature and composition of pig iron are introduced manually into the system.

Static automatic control systems are also employed in the USSR for controlling oxygen converter operation. The systems may also use other methods for stopping the blow at a specified carbon content, for instance, by measuring the radiance of flame or the amount and composition of waste gases. The radiance of flame is detected by a radiation sensor. The computation of the actual carbon content from the content of CO and CO_2 in the converter gases (determined by optico-acoustical analyzers) is performed by an analogue computer type "Uglerod K" developed at the Automation Institute of Kiev.

Computations by the main algorithm are made by means of the УМШН computer using the principal data introduced into the machine from the sensors via the data collection and conversion system, part of these data being introduced manually by a key input device.

Figure 69 shows the circuit for automatic control of converter operation. The machine is supplied with the following information: amount of pig iron (measured by electronic tensometric scales); amount of steel scrap (introduced manually with the aid of the key input device); amount of loose additives (automatic input); temperature of hot metal and final steel (measured by a vacuum quantometer); composition of iron ore and lime (manual input); purity of oxygen (automatic input); flow rate and total

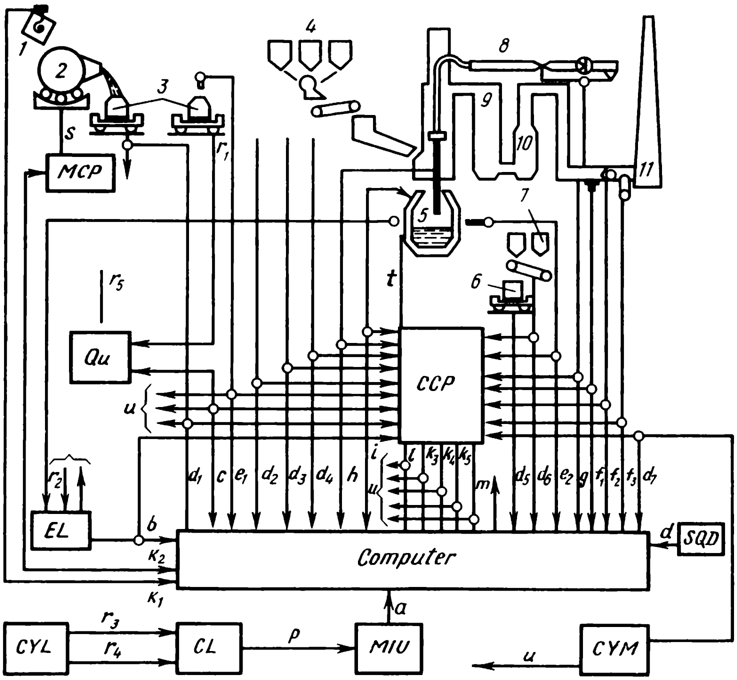


Fig. 69. Structural diagram of automatic control of a Bessemer converter

1—iron-pouring ladle; *2*—mixer; *3*—iron ladle; *4*—loose materials bunkers; *5*—converter; *6*—teeming ladle; *7*—bunkers for alloying and deoxidizing materials; *8*—oxygen supply line; *9*—waste-heat boiler; *10*—dust-collecting plant; *11*—stack; a—data supplied manually to the computer (number of heat, grade of steel, steel mass, composition of iron ore, lime and scrap, content of Fe_{tot} in slag); b—information from express laboratory (EL) on steel analysis; c—data from quantometer Qu (analysis of pig iron and steel after deoxidation); d—data from the shop's quality control department (SQD) (purity of oxygen); d_1-d_7—data on the mass of component (d_1—iron, d_2—iron ore, d_3—bauxite. d_4—lime, d_5—steel, d_6—deoxidants and alloying additives, d_7—scrap); e_1—temperature of iron; e_2—temperature of steel; f_1—composition of waste gases; f_2—flow rate of waste gases; f_3—temperature of waste gases; g—pressure and flow rate of oxygen; h—position of the lance; i—flame radiance above the converter neck; k_1-k_5—computer output data to converter control panel (CCP) and mixer control panel (MCP) on the amounts of materials required for the heat; k_1, k_2—pig iron, k_3—iron ore, k_4—lime, k_5—deoxidants and alloying additives; l—computer output data on the amount of oxygen for the heat; m—data on the current carbon concentration in the bath; p—data supplied from the central laboratory (CL) to the manual input unit (MIU) (compositions of iron ore, lime, and slag); r_1-r_5—data on chemical composition of samples (r_1—pig iron, r_2—steel, r_3—iron ore, r_4—lime; r_5—steel after deoxidation); s—position of the mixer; t—position of the converter; u—data transmission to other converters; CYM—charging yard of magnetic materials; CYL—charging yard of loose materials usage of oxygen (automatically measured by a flowmeter and integrator); oxygen pressure; setting of the lance; and express analysis of steel (according to the data from vacuum quantometers, carbometer or styloscope, introduced manually with

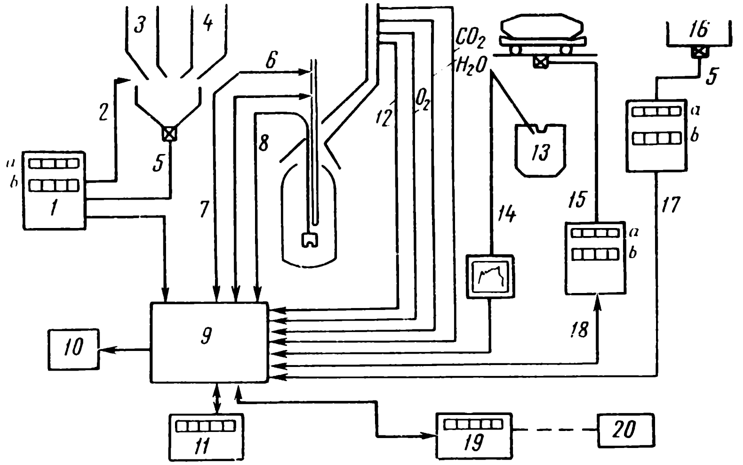


Fig. 70. Principal diagram of controlling the oxygen converter heat

1—flux weighing control; *2*—instruction to the weighing bunker; *3*, *4*—loose materials; *5*—scales; *6*—oxygen flow rate control; *7*—lance control; *8*—bath temperature; *9*—computer unit P-50; *10*—typewriter; *11*—control panel; *12*—waste gas flow rate; *13*—liquid iron; *14*—iron temperature; *15*—iron mass; *16*—scrap mass; *17*—scrap weighing control; *18*—iron weighing control; *19*—chemical analysis; *20*—spectrometer; *a*—actual mass of the melt; *b*—specified mass of the melt

the key input device). The temperature of steel at the end of the blow is measured by an immersion thermocouple, the result being introduced into the machine. The moments of the start of blow and of tapping are recorded automatically.

Figure 70 shows the principal diagram of dynamic control of the oxygen converter process. The system also provides for static control with the use of the algorithm of the mathematical model of the process, as described above, but is additionally provided with a feedback circuit. Dynamic control is employed during the last few minutes of the blow to make required corrections to the current parameters of the process in order to produce steel of specified composition and temperature.

Other systems of automatic control of oxygen-converter operation also exist. Automatic control of converter heats makes it possible to finish the operation more accurately, increase the productivity of converters, and improve the technico-economical indices.

DEOXIDATION OF CONVERTER STEEL

Oxygen converters mostly have a special notch for tapping metal, which almost excludes mixing of metal and slag, reversion of phosphorus from slag to metal on addition of deoxidants to the ladle, and also boiling of the metal in the ladle and splashing of slag, and is favourable in decreasing the loss of deoxidants.

Rimming steel is commonly deoxidized during tapping by adding a specified weight of ferro-manganese to the jet, the size of manganese lumps being not more than 100 mm. The consumption of ferro-manganese is not high, since reduction of manganese from slag to metal is always observed in oxygen converter processes.

Killed steels are deoxidized in accordance with the specified carbon content. For instance, high-carbon rail steel (0.65-0.74 per cent C, 0.6-1.0 per cent Mn, and 0.27-0.30 per cent Si) is deoxidized in the following manner: the blow is stopped at 0.57-0.63 per cent C in the metal. The specified solid deoxidants, such as ferro-manganese, ferro-silicon, and aluminium are introduced into the ladle in the order indicated. In heats with overblow, dried anthracite is additionally introduced into the ladle.

For deoxidation and alloying of low-alloyed and medium-alloyed steels, preliminary slagging-off is obligatory. Low-alloyed steel Grade 25Г2С (0.20-0.29 per cent C, 1.2-1.6 per cent Mn, 0.6-0.9 per cent Si, less than 0.05 per cent S and less than 0.05 per cent P) is deoxidized as follows. The blow is stopped when the carbon has dropped down to 0.1-0.12 per cent, and at least two-thirds of the total bulk of slag is poured off from the vessel through its throat, after which the metal is tapped through the notch, with ferro-manganese and 75-per cent ferro-silicon being added to the jet of steel. If 45-per cent ferro-silicon is used, one-third of its specified amount may be put into the ladle prior to tapping. Aluminium in lumps roughly 50 mm in size is then added (500 g per ton steel). All additions are loaded in the ladle until the level of metal in it reaches one-half of its height, i.e., until slag appears in the ladle.

Deoxidation and alloying of steel Grade 10ХСНД (СХЛ-4) are made by charging the required additions (to provide for 0.70 per cent Ni and 0.55 per cent Cu in the final steel) into the vessel before pouring in pig iron, the mass of the metallic charge and the content of these elements in the scrap being taken into account. The blow is stopped at 0.07-0.08 per cent C in the metal. Upon slagging-off of at least two-thirds of the bulk of slag from the vessel, low-carbon ferro-chrome (0.05 per cent C and 0.71 per cent Cr) is added to diminish the loss of chrome and deoxidants and the reversion of phosphorus from slag to metal. Upon loading ferro-chrome, the vessel is rocked for 3-4 minutes to equalize the composition of the melt.

During tapping, 75-per cent ferro-silicon (a part of its specified amount being put into the ladle prior to tapping), manganese metal, aluminium, and ferro-titanium are added to the metal flow. When making alloyed steel, it is advisable to put exothermic ferro-alloys (either fluxed or unfluxed) into the ladle, which can shorten the tap-to-tap time. This is of high importance, since high-carbon low- and medium-alloyed steels require more time for melting because of the need to deoxidize them. A still better choice are molten ferro-alloys which are poured into the metal flow during tapping.

Semi-killed steel is deoxidized in the ladle by ferro-manganese and 45-per cent ferro-silicon charged in such an amount as to have 0.07-0.10 per cent Si in the metal after its oxidation. The final corrections in the deoxidation of steel are made by adding granulated aluminium (30-100 g per ton steel) into moulds or the central runner (in bottom pouring).

Because of the high productivity of converters, care should be taken to finish the teeming and remove ingots in the moulds from the shop as soon as possible. For that reason, converter steel is predominantly cast into large ingots.

When teeming rimming steel, especially by express-methods, this may result in a weak boiling of the metal in moulds, owing to a low degree of oxidation and high manganese content of the metal and also a large height of moulds. Boiling in moulds can be intensified by employing certain intensifiers (mill scale and soda) or by blowing oxygen into the jet of the metal being teemed. In some cases, making chemically capped or semi-killed steel instead of the rimming kind may be a way out of the situation.

Industrial experiments have been successfully carried out at the Novo-Lipetsky and Donetsky works on combining oxygen converters with continuous slab-casting plants, the operation being done by the "melt after melt" method with the metal cast from 170- to 250-ton ladles. The results obtained are very promising, since by standardizing the billets cast and combining the continuous casting plants with reducing mills, it will be possible to appreciably increase the productivity. Experience in combining oxygen converters with continuous casting plants has also been gained at some works in other countries.

In the oxygen converter process, manganese reverts from slag to metal by the end of the melt, which is also indicative of a low oxidation of the bath. Even if the MnO content of the metal is low, deoxidation of steel with silicon will result in combining this impurity into a fusible compound $2MnO \cdot SiO_2$ which is quite easily picked up by the slag. For that reason, steel produced by the oxygen converter process is undoubtedly of a better quality than open-hearth steel for the same manganese content of the charge.

The lower the content of FeO and SiO_2, the greater the concentration of active CaO in the slags, and the higher the temperature, the more successful is the removal of sulphur in both oxygen converters and open-hearth furnaces. Part of sulphur (6-10 per cent of its total amount in the melt) is removed with gases. High-basic free-running slags quickly formed in the converter in the reaction zone under the oxygen torch are beneficial for the removal of sulphur and the sulphur content of the steel produced is not higher than that of the open-hearth steel.

As is known, the final converter steel contains 0.003-0.005 per cent nitrogen, depending on the purity of oxygen and the tapping time (not less than 3 minutes for a 130-t melt), against 0.0040-0.0075 per cent nitrogen in the open-hearth steel. According to some data, converter steels are also lower in hydrogen.

Thus, despite some critical views, converter steels, are by no way inferior to open-hearth steels.

As has been found by comparative tests of oxygen-converter and open-hearth carbon steels at room (+20°C) and subzero (—40°C) temperatures, the mechanical properties of the former steels are not worse and sometimes better than those of the latter.

Converter steels are low in non-metallic impurities, possess a high resistance to brittle fracture at subzero temperatures (in tensile tests of specimens with stress concentrators), a low liability to spot hardening in welding, and a low liability to the formation of fissures on heating. Chrome-nickel-silicon-manganese-copper steel 10ХСНД (СХЛ-4), after being successfully tested by various methods, was recommended for use in the shipbuilding industry. As to its ageing, suitability for industrial use, weldability, strength of weld seams, and critical brittle point, this steel is not worse than the comparable open-hearth steel.

Low-alloyed converter steel 35ГС is not inferior to the respective open-hearth grade and retains its high impact strength at subzero temperatures. The point of cold brittleness of this grade, either converter or open-hearth made, is between —40° and —60°C.

High-quality carbon steel Grades 10 and 20 for tube rolling was produced in oxygen converters. Broaching and rolling of tube stock of this steel were as easy as with open-hearth steels. The yield of first grade tubes was 98 per cent. The mechanical properties of the steel were mostly above specified values.

Semi-killed steels produced by the oxygen converter process were also found to have the same quality as open-hearth grades.

Correct deoxidation and alloying of converter steel in the ladle, an ample amount of heat for quick and full melting of the ferro-alloys added into the ladle, and intense mixing of metal and slag by the jet of metal falling down from an appreciable height — all these factors speed up the desired reactions and promote coalescence, coagulation and removal of reaction products to the metal-slag interface, where they are picked up by the slag. This results in a better quality of the steel produced. Oxygen converters are now employed with success for making carbon steels, structural steel for Isteg reinforcing rods, rail steel, tube steel, semi-killed medium-hard steel, steel grade 08 кп for deep drawing, low-alloyed steel grades 10ХСНД (СХЛ-4), 10ХГ2С, 09Г2Т, etc. The assortment of low-alloy steels produced in oxygen converters will be widened after industrial application of the methods of deoxidation by molten ferro-alloys, exothermic ferro-alloys, and fluxed exothermic ferro-alloy briquettes.

PRINCIPAL TECHNICO-ECONOMICAL INDICES OF OXYGEN CONVERTER PROCESS

Technico-economical indices determining the efficiency of an oxygen-converter shop include the following: productivity of converters, service life of converter lining, consumption of pig iron per ton of steel (can be reduced by replacing some pig iron with cheaper scrap), consumption of refractories, yield of ingots, labour productivity, and cost of steel.

The duration of the converter heat (tap-to-tap time) comprises the blow time and the time required for auxiliary operations. The blow time may be shortened by intensifying the blast, i.e., supplying more oxygen per minute per ton of the metallic charge. This, however, can only be done to a definite limit determined by the capacity and shape of the vessel and the iron-to-scrap ratio in the melt.

The yield of final ingots is dependent on the yield of liquid steel. The more pig iron is used in the melt and the higher is the content of impurities in the iron, the lower is the yield of liquid steel. On the contrary, using more scrap in the charge increases the yield of liquid steel. Some metal is lost with splashes, ladle skull, short run castings, in risers and bottom gates. If iron ore or mill scale is used in the process, some of the iron (roughly 50 per cent of the total iron content) is reduced to metal.

The yield of steel is calculated by dividing the mass of sound ingots by the total amount of pig iron, scrap and deoxidants used in the melt plus 50 per cent of the iron contained in iron ore or mill scale (when added). For instance, a 100-ton vessel is charged with 82 tons of pig iron and 28 tons of scrap to make rimming steel; 4 ton iron ore (60 per cent Fe) is used for slag formation; the metal in the ladle is deoxidized with 600 kg ferro-manganese. The mass of the metallic charge, taking into account 50 per cent of the iron in the iron ore, is $82 + 28 + 0.6 + 4 \times 0.6 \times 0.5 = 111.8$ tons. The mass of sound ingots is 100 tons. The yield of sound ingots therefore is $(100 : 111.8) \times 100 = 89.4$ per cent, and the metallic charge to make one ton of sound ingots is $111.8 : 100 = 1.118$ tons. As can be concluded from this example, a charge containing more pig iron and less scrap, all other things being the same, will give less than 100 tons of sound ingots, since more impurities will be burnt off from the larger mass of pig iron. The mass of the metallic charge per ton of sound ingots will therefore be greater.

For that reason, the principal trend in the development of the oxygen converter process must be an increase of the proportion of scrap in the charge.

New processes are being developed in which the relative mass of scrap is appreciably increased. At some works, scrap is preheated in the vessel to 680-720°C by using gaseous, liquid or solid fuel (coke, silicon and calcium carbides). Experiments were carried out on running oxygen-converter melts with the use of 50 per cent solid open-hearth iron in the charge and also 32 per cent scrap preheated in the vessel by liquid fuel. Experimental melts in a 200-ton oxygen converter proved it possible to melt as much as 51 per cent scrap in the charge by using calcium carbide (4.5 per cent of the mass of the metallic charge). The process with scrap preheating is however uneconomic, since the expences turn out to be 15 per cent higher and the labour productivity, 5 per cent lower than in the ordinary oxygen converter process.

The cost of ton of steel is estimated from the cost of metallic charge (pig iron, scrap, lime, limestone, mill scale, etc.), lining refractories, oxygen, steam, compressed air, electric energy; expenses on repairs of vessels, ladles, stoppers, teeming devices, ferro-alloy furnaces, on current repairs of converters and related equipment; cost of replaceable equipment (moulds, bottom plates, charging boxes, chutes, slag pots, etc.); cost of load-transportation service offered by auxiliary shops; cost of auxiliary materials; wages, salaries and extra pays of the shop's personnel; and depreciation of the shop's equipment.

The sum of all these expenses for a certain period, say, a month, divided by the mass of sound ingots produced during that period, gives the cost of one ton of sound ingots. To reduce it is the task of prime importance. This may be achieved by lowering the expenditures on any of the items enumerated. But, if we carefully analyze the items constituting the cost of ton of ingots, we may see that the largest among them is the cost of the metallic charge and, in particular, the cost of pig iron. It then follows that the prime objective must be to raise the proportion of scrap in the charge and to lower that of pig iron.

The most important index of the operation of a converter is its productivity (annual, daily or hourly), which can be increased by increasing the mass of the charge. Raising the converter productivity reduces the cost of steel, since the so-called fixed expenses of the shop (depreciation, equipment repairs, and general expenses of the shop or the works) are deducted all the same from the shop's gross profits irrespective of the amount of steel produced in a given converter.

Another means for reducing the cost of steel is to lower the expenditure on current repairs, in particular, to prolong the service life of the vessel lining.

The cost of conversion includes all the expenses required to convert the metallic charge into steel. As has been found from the analysis of all these expenses on process fuel, power supply, replaceable equipment, current repairs, and maintenance of the shop's equipment, and general expenses of the works and the shop including wages and extra pays, the cost of conversion in oxygen converters is 5.09 roubles per ton steel, i.e., 25 per cent lower than in a modern open-hearth shop.

Some technico-economical indices of operation of modern oxygen-converter shops with top-blown oxygen converters are given below.

Conversion of Open-hearth Pig Iron

Converter capacity, t	100-300
Blow time, min	15-18
Tap-to-tap time, min	30-50
Annual output of the shop, mln ton ingot steel:	
with three 100-ton converters	2.5-3.0
with two 250-ton converters	2.5-3.0
Metal yield, %	89-92
Lime used, %	6-10
Scrap used, %	18-27
Oxygen consumption, m^3 per ton steel	50-56
Consumption of refractories in vessel lining, kg per ton steel	2.0-4.0
Lining life, heats	400-800
Cost of conversion, roubles per ton steel	5-8

Conversion of High-phosphorus Pig Iron

Converter capacity, t	20-180
Blow time, min	18-28
Tap-to-tap time, min	50-65
Metal yield, %	87-89
Lime used, %	10-16
Scrap used, %	20-35
Oxygen consumption, m^3 per ton steel	60-63
Lining life, heats	120-450

The capital costs of construction of an oxygen-converter shop are 17-20 per cent lower than those for an open-hearth shop of a comparable annual output. The labour productivity in an oxygen-converter shop is 25-27 per cent higher and the cost of steel 2-3 per cent lower than in an open-hearth shop. An essential feature of the operation of oxygen converters is a very high annual productivity.

Thus when compared with the open-hearth steel manufacture, the manufacture of steel by the oxygen converter process is characterized by lower capital and operational expenses per ton steel, a higher productivity of units, and a higher labour productivity. High technico-economical indices and large possibilities for mechanization and automation of work ensure further development of the oxygen converter process.

Chapter Eleven

ORGANIZATION OF WORK IN OXYGEN CONVERTER SHOPS

LAYOUT OF OXYGEN CONVERTER SHOPS

The annual output of a modern oxygen converter shop with large-size converters reaches 2.5-6.0 mln ton steel. To ensure such an output, special measures are required, in particular, a rational layout of the shop, correct organization of loads transportation in all its departments, strict distribution of production operations among shop's departments and coordinate work of the operators and engineering personnel and their observance of technological instructions and labour protection and safety rules at each working place and in each department.

The principal paths of loads transportation in an oxygen converter shop include the routes for supplying molten iron, solid charge materials, liquid steel, moulds, refractories, and for removing ingots, slag, broken refractories, and wastes. Intersections between these paths should be avoided where possible. To ensure smooth operation it is necessary to provide individual handling machinery for each of the main transportation paths. Overhead cranes should be used only for lifting and transverse carriage of loads, and railway, automobile or monorail transport for carrying loads along the shop.

An essential feature of the oxygen converter process is a high frequency of tappings, which is due to a very short time of the converter cycle (30-40 min). When two out of three converters in the shop are run simultaneously, their independent operation must be fully ensured.

Each kind of material should be conveyed to and charged in the vessel by appropriate mechanisms at such speeds that the time of charging of solid materials and of pouring-in of pig iron can be not more than 10-15 per cent of the total tap-to-tap time.

In oxygen converter shops steel is teemed by direct pouring or uphill teeming into ingots of various mass according to the requirements of the rolling mills. Combining the operation of oxygen converters with continuous casting plants becomes popular; this helps facilitate the labourious work of steel casting and automatize many operations.

A standard converter shop developed by the Gipromez Institute for three oxygen converters of a capacity of 100-130 tons and 250 tons and an annual output respectively of 2.5-3.0 mln tons and 6.0 mln tons of ingots (Fig. 71) has the following departments: a converter department with three converters; two casting departments; mixer department (two 1300-ton mixers); department of magnetic charge materials; department of loose charge materials (or the work's store of loose materials); department of hydraulic cleaning of moulds; sprays for cooling moulds; mould-dressing yard; mould-train preparation yard; and stripper yard.

The converter department is located in a closed building consisting of four bays; a charging bay, a converter bay, and two casting bays. All four bays are connected by railway lines passing beneath the converters, for transporting steel and slag.

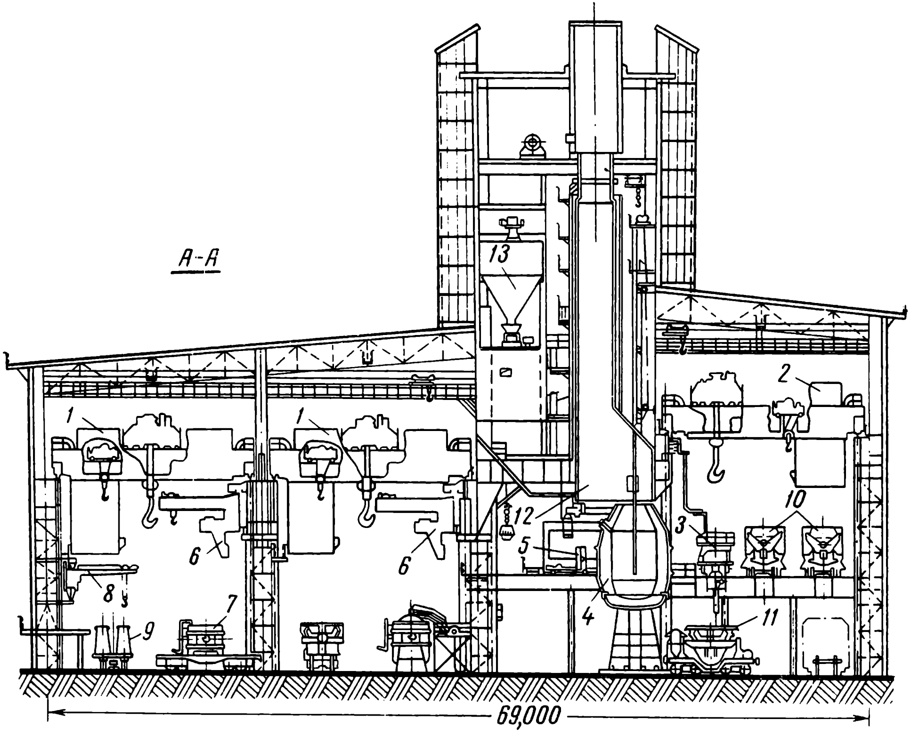
PRINCIPLES OF MAKING UP THE SCHEDULE OF OPERATION OF A CONVERTER SHOP

To attain the planned productivity of a converter shop, it is very important to organize the operation so that the heats can follow each other without large intervals, which is easier to achieve if the pig iron used does not vary much in its chemical composition and temperature, and the conditions of slag formation, blast and also temperature conditions during the heats are maintained stable. These parameters are the principal ones and if they are properly controlled, the blow time and tap-to-tap time will vary only insignificantly, thus enabling the rhythmic operation of the converters and the whole shop.

The tap-to-tap cycle includes the operations of scrap charging, pig iron pouring, blowing, sampling and sample analysis, measurements of metal temperature, control of the temperature and carbon content of the melt (when

Fig. 71*a*. Cross-sectional view of a standard converter shop with 100-130-ton converters

1—teeming crane; *2*—iron-pouring crane; *3*—carriage for charging scrap into converters; *4*—converter; *5*—sampling stage; *6*—cantilever crane; *7*—teeming ladle carrier; *8*—3-ton cantilever crane; *9*—mould train; *10*—iron ladles; *11*—slag pot; *12*—waste-heat boiler; *13*—loose materials bunker



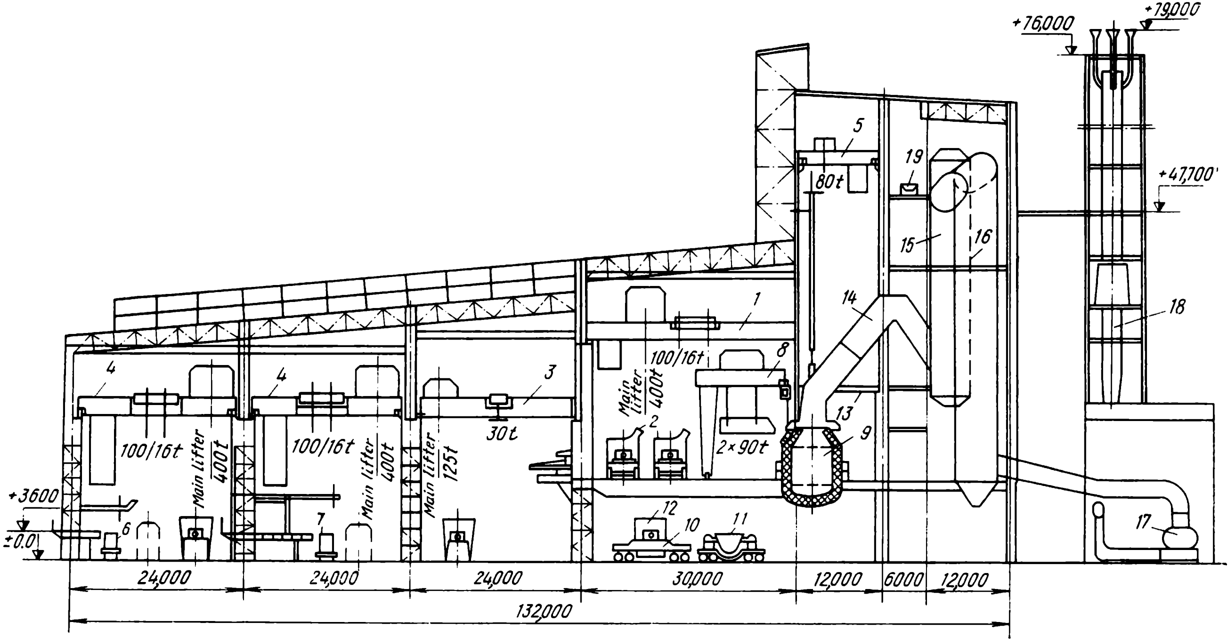


Fig. 71*b*. Cross-sectional view of a standard oxygen converter shop with 250-ton converters

1—iron-pouring crane; *2*—iron ladle; *3*—auxiliary cranes; *4*—teeming cranes; *5*—crane for moving the lance; *6*—mould train; *7*—ditto; *8*—charging crane; *9*—converters; *10*—teeming ladle carrier; *11*—slag pot; *12*—teeming ladle; *13*—chimney-moving stage; *14*—waste-heat boiler; *15*—coarse gas cleaning; *16*—fine gas cleaning; *17*—exhauster; *18*—stack; *19*—belt conveyer for loose materials needed), tapping, and removal of slag from the converter. After each tapping, the converter is inspected and its neck, tap-hole, and lining are repaired if required.

The operational schedule is drawn up for the whole tap-to-tap cycle with due regard for the sequence of operation of the converters, the time of delivery of pig iron to the mixer and from the latter to the converters (or mixer ladles), the time of delivery of tapping ladles and slag pots, and the time of transportation of the ladles to continuous casting plants. The time required for delivery of scrap and pig iron to the converters, replenishment of bunkers with loose materials, tapping and teeming of steel, removal of waste, and for other operations indispensable for normal work of the shop must also be taken into consideration.

The schedule must include planned stoppages of the converter for preventive repair which cannot be made during the heats and also for complete relining of the converter. Relining is usually done in place, but small-size oxygen converters may be transferred for repairs to a special stand.

Reliable communication between the individual departments and the control panel is of importance for proper work of the shop. All the departments of the shop are usually provided with the telephone service. In addition, the control panel dispatcher can transmit instructions and make announcements by radio. The converter shop communicates through the dispatch switch board with blast-furnace shop, mixer department, stripper department, scales room, soaking pits of the roll mill shop or continuous casting plants, transportation service, laboratory, works management, etc.

Before every shift-over, the necks of all operating converters must be cleaned of skull and coated with clay and their hoods cleaned of skull and slag. Slag and waste must be removed from beneath the converters. Skull must also be removed from lances and steel ladles. Skull is to be collected into charging boxes and removed from the shop.

WORK ORGANIZATION IN AN OXYGEN CONVERTER SHOP

We shall consider, as an example, the organization of work in a shop with three 100-ton converters. Liquid iron is delivered from the blast-furnace shop to the mixer department of the converter shop in iron ladles of a capacity of 100 or 140 tons. The iron is poured from the mixer into 140-ton iron ladles, in which it is simultaneously weighed. The filled ladles are transported by a diesel locomotive to the charging bay of the converter department and the iron is poured into the converters by means of an overhead crane.

In the USA, Japan, and Western Europe, mixer ladles are finding ever wider use for transportation of pig iron to converter departments. They have certain advantages, e.g. the mixer department may be dispensed with, the iron poured into converters has a higher temperature, etc. But the iron must meet more rigorous requirements as regards its composition, since it cannot be made uniform here as it can in a mixer.

Scrap is delivered from the scrap preparation department to the charging bay of the converter shop in large boxes placed on railway flat cars. After partial sorting and weighing, the scrap is delivered by self-moving cars to the converter department and loaded by overhead cranes into the converters. Light-weight scrap may be charged into converters by iron-pouring ladles. Other methods for charging scrap are also in use. For instance, scrap may be transported from the charging bay to converters in boxes placed on railway carriages, the train of carriages being moved along the converters during charging of scrap by means of a pusher carriage. When the axis of a box is made coincident with that of the converter neck (the latter being turned down), the rod of the charging machine turns the box around its axis and the scrap falls into the converter. This, however, is an outdated and inefficient method. Rapid charging of vessels is now made by using cranes with large-capacity boxes. In that case the whole amount of scrap required for a melt can be charged in one pass. Thus, with a box of a capacity of 65 tons the time of charging scrap is only 1 minute.

Loose materials (iron ore, lime, bauxites, fluorspar) are delivered from the department for loose materials into the bunkers of the converter department by means of a system of belt conveyers. The number of bunkers mounted above the converters corresponds to the number of various materials to be employed in the process and also to their quantity to be consumed. For instance, each 100-ton converter has 4-6 bunkers, each 250-ton converter, eight bunkers or sometimes even more.

Materials from these bunkers are fed to a weighing device and then brought by a belt conveyer to an intermediate bunker, from which they are charged into the converter as soon as needed. All the operations regarding the delivery, weighing, and charging of loose materials into converters are fully mechanized and automatized. Ferro-alloys are stored in the charging bay in storage bunkers, from which they are delivered to intermediate bunkers.

The intermediate bunkers installed at each converter serve to discharge the required amount of ferro-alloys into teeming ladles. These bunkers are provided with tiltable funnels. Ferro-alloys are brought from the intermediate bunkers via a belt conveyer to the funnel and then via a chute, into a ladle.

A water-cooled lance for supplying oxygen into the vessel is provided with a three- or four-nozzle end piece. It is fastened by two parallel chains to a carriage and moves together with the latter along vertical guides. The rated speed of motion of the lance is 1 m/s, but a lower speed of 0.2 m/s may be used for more accurate positioning of the lance. Each converter is provided with a second spare lance, which is always kept fully prepared for operation. The lance can be lifted automatically at a speed of 2 m/s and the supply of oxygen to it cut off in emergency cases, for instance, when the pressure of oxygen drops sharply or the temperature of cooling water increases appreciably.

The final steel from a 100-ton converter is tapped into a 130-ton teeming ladle placed on an electrically driven remote-controlled carriage. The carriage can move along a transverse railway laid at the level of works floor into either of the two teeming departments.

Slag from converters is poured into slag pots placed on carriages. Slag pots are filled with slag to a specified level and then moved by diesel locomotives to the slag yard.

Each teeming department has two overhead travelling cranes of a load-carrying capacity of 180/50 t which carry teeming ladles to teeming stages.

After a certain lapse of time predetermined for each grade of steel being made, metal-filled moulds are transported to the stripper department located in a separate building. Ingots of killed steel are extracted from moulds (or, in the case of rimming steel, moulds are stripped from ingots) and delivered to soaking pits of rolling mills. Free moulds are cooled in air and then transported to the department of hydraulic mould cleaning.

Moulds of various types and sizes are cleaned in a hydraulic installation provided with nozzles. A nozzle is introduced into a mould and lowered and lifted there for less than one minute, during which time the mould is cleaned of clay, tar and dirt by the water supplied from the nozzle at a high pressure (up to 60 at). The train of moulds is moved during cleaning by a pusher.

After hydraulic cleaning, the train of moulds is transferred to the dressing department, where the inner surface of moulds is dressed (coated) with varnish or tar. The temperature of moulds before dressing must be 70-90°C. The process of dressing is mechanized by using dressing machines disposed over the railways on which the train of moulds moves. Varnish or tar is supplied through a nozzle which is periodically lowered and lifted, so that the walls of the mould are coated completely with the dressing material during this cycle.

Dressed moulds are transported to the mould yard where mould trains are assembled for teeming. Moulds are placed by a crane on bottom plates and are then covered with hot tops. Hot tops and central runners are prepared for teeming in the mould yard. The layout and equipment of the mould yard are determined by the method of teeming (either direct or uphill) and the weight of ingots.

The mould yard is provided with movable platforms which are transferred over the railways for mould trains. If the method of uphill teeming is adopted in the shop, mould trains are assembled by the flow method, i.e., bottom plates are cleaned and assembled in a preparatory section and moulds are placed on the prepared bottom plates in an assembling section, the trains being moved from the first to the second section by a capstan. The prepared mould trains are moved from the mould yard to branch tracks and then to the casting bays of the converter shop.

If the method of continuous casting of steel is employed in the shop, the operational scheme is somewhat different. The teeming ladle with metal is lifted by an overhead crane to the working stage of a continuous casting plant and is set above a tundish, after which the metal is poured into the latter. When the metal in the tundish rises to a height of 650 mm, the stoppers of the tundish are lifted and the metal is poured into a water-cooled mould. When the metal in the mould reaches the specified height, the drive mechanism of pinch rolls is switched on and the dummy bar and the partially solidified billet begin to move downwards. In the course of pulling, the dummy bar is detached and the solidified billet is cut into pieces of specified lengths, which are delivered by a mechanism to a roll table positioned at the shop floor level and transported by the latter into the roll mill shop.

GAS CLEANING IN OXYGEN CONVERTER SHOPS

As has been mentioned earlier, iron evaporates in oxygen converters because of a very high temperature developed in the reaction zone (2500-3000°C). Iron vapours oxidize and a part of them which has not settled down in the slag and foam is carried off by the gases as finely dispersed dust (particle size 0.05-1.5 microns). The result is that a large amount of gases is formed during converter heats, especially in large-size converters (70-80 m^3 per ton iron or approximately 8000 m^3 during a heat of a mass of 100 tons, i.e., roughly 20000 m^3/h). The average dust content of these gases is 28-50 g/m^3, but may be as high as 120 g/m^3 during some periods of the heat. The amount of dust reaches 1-2 per cent of the mass of the metallic charge. The gases evolved are reddish brown in colour because of the presence of a large amount of iron oxides.

The content of dust in waste gases increases with temperature. The average composition of the dust is as follows: 65 per cent Fe, 1.0-1.25 per cent SiO_2, 3.5-4.5 per cent MnO, 0.5-1.0 per cent Al_2O_3, 0.3-0.4 per cent CaO, 0.32-0.38 per cent P_2O_5, and 0.10-0.15 per cent MgO.

The composition of the gases may vary substantially during the heat, a typical composition being 40-80 per cent

CO, 8-35 per cent CO_2, 0.5-5.0 per cent O_2, 0.5-3.5 per cent H_2, and 5.0-11.0 per cent N_2. As is seen, the main component is carbon monoxide. The heat of combustion of the gas may vary between 2250 and 2450 kcal/m^3 depending on the content of CO in the gas. The waste gases can be utilized for chemical synthesis or as fuel.

Because of the high dispersity of dust and the high temperature of waste gases (1600-1700°C), their efficient cleaning is linked with certain difficulties. In modern practice the problem of dust collecting is solved by either of the two methods:

(1) the combustible components of the gas are afterburned by supplying some air and the gas is then cleaned from dust;

(2) the gases are removed without afterburning, for which purpose they are withdrawn through air-impermeable gas ducts and then, after cooling and cleaning, are supplied to gas holders for further utilization.

Thus, both methods are based on cooling the gases before delivering them into a gas-cleaning device. The cooling proper may be carried out either with or without heat utilization. In the former case, the gases are cooled by burning them in a large volume of cold air, which is sucked in through the gap between the converter neck and chimney, and also by spraying water. This method is predominantly used in the USA and Canada, often without water spraying. A disadvantage of the method is a large amount of gases formed (up to 150-160 m^3 per ton iron), and therefore a large rated power of exhaust fans and a high consumption of electric energy required.

When gases are cooled with afterburning and heat utilization, the amount of air supplied is not large. Water is sprayed in by this method too. The heat evolved is utilized in waste-heat boilers of radiation or radiation-convection type. An installation operating by this method is shown in Fig. 72. Air is supplied in such an amount that the excess air ratio is not higher than 2.5. The boiler plant also serves for preliminary coarse cleaning and cooling of the gases.

A number of steelmaking works in France, the Federal Republic of Germany, Japan, and Belgium employ the method of gas cleaning without afterburning in the chimney, which makes it possible to reduce the size of the gas-cleaning installation and use smaller-power fans, besides, it facilitates gas cleaning and allows further utilization of the chemical heat of gases. An installation developed by the CAFL

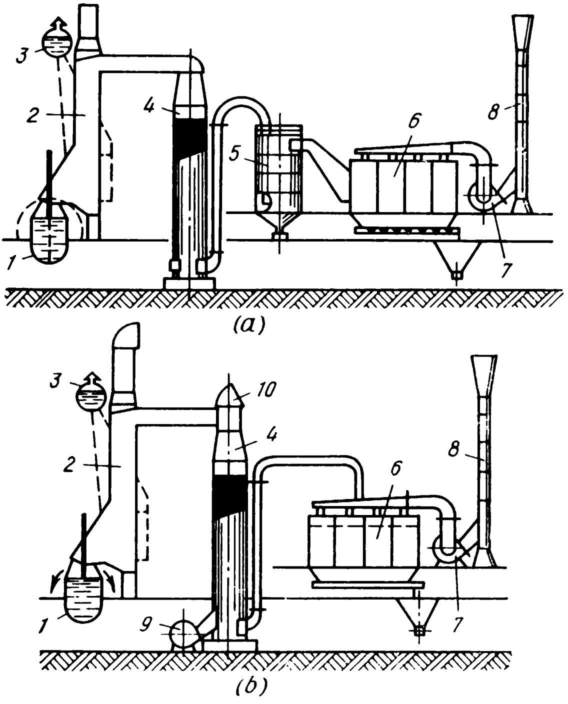


Fig. 72. A plant for heat utilization and cleaning of converter gases using a regenerative heat exchanger

a—layout with a scrubber; *b*—layout without a scrubber; *1*—converter; *2*—chimney with a radiation waste-heat boiler; *3*—boiler drum; *4*—regenerative heat exchanger; *5*—scrubber; *6*—cloth filter; *7*—exhaust fan; *8*—stack; *9*—fan for blowing the heat exchanger; *10*—release valve

Co., France, for operation by this method is shown in Fig. 73. The gases are supplied to waste-heat boilers mounted inside the chimney, and then to a gas scrubber, after which they are delivered to a gas holder. Air inleakage is prevented by forming a certain excess pressure in the converter neck, providing a sealing chamber, or forming a steam screen between the chimney and converter neck. As has been found, the operation of 125-140-ton converters with a slightly increased gas pressure under the hood reduces splashing and increases the yield of steel by 10-15 kg per ton. The dust content of gases after cleaning in the installation lowers from 120 g/m^3 to 0.1 g/m^3. As distinct from the method with gas afterburning in which the converter dust contains mainly Fe_2O_3 and Fe_3O_4, the dust formed in the method without afterburning, contains 75% Fe, 20% FeO and 5% Fe_3O_4. This dust settles down more readily.

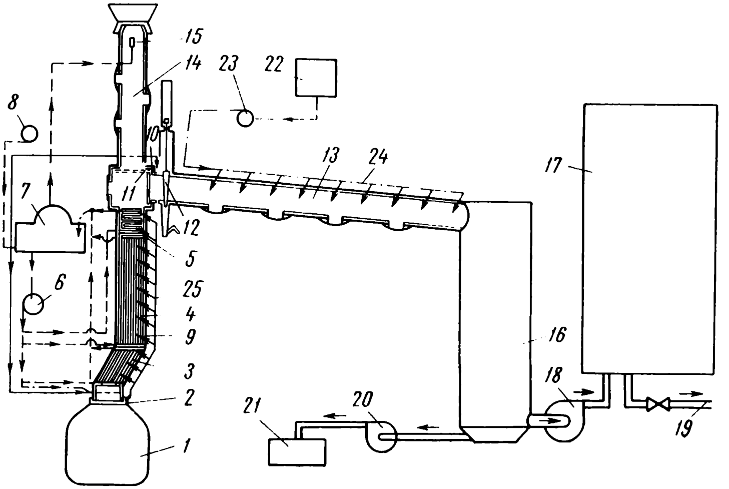


Fig. 73. Layout of a CAFL installation for converter gas cleaning without afterburning

1—converter; *2*—sealing chamber; *3*—1st circulation contour of the waste-heat boiler; *4*—2nd circulation contour of the waste-heat boiler; *5*—3rd circulation contour of the waste-heat boiler; *6*—circulation pump; *7*—boiler drum; *8*—feed-water pump of the boiler; *9*—chimney; *10*—sealing chamber; *11*—control valve; *12*—gate valve; *13*—gas duct; *14*—stack; *15*—steam ejector; *16*—scrubbing dust collector; *17*—gas holder; *18*—exhauster; *19*—converter gas supply to consumers; *20*—sludge pump; *21*—sludge separator; *22*—water tank; *23*—pump; *24*—supply of water for atomization; *25*—supply of steam for blowing out the screen pipes of the boiler

A method of gas removal without afterburning and with the use of a nitrogen screen (the so-called OG system) is widely employed in modern practice. An installation using this method developed by the Baumco-Demag Co. is shown in Fig. 74. The lower portion of the chimney is provided with a sealing ring which is lowered onto the converter neck by a hydraulic mechanism, the gap between them being sealed by a screen of gaseous nitrogen. The gases are cooled in a waste-heat boiler down to 350°C and after scrubbing and drying are directed to a gas holder or discharged into the atmosphere.

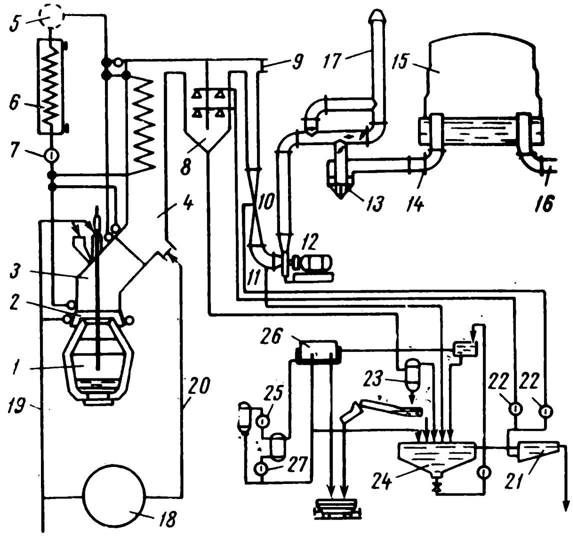


Fig. 74. Layout of an installation for cleaning of converter gases without afterburning

1—converter; *2*—annular pipe for supplying nitrogen; *3*—water-cooled chimney; *4*—coils; *5*—collector; *6*—heat exchanger; *7*—circulation pump; *8*—scrubber-evaporator; *9*—safety valve; *10*—atomizing pipe; *11*—separating bend; *12*—exhauster; *13*—water gate; *14*—pipe for gas removal to gas holder; *15*—gas holder; *16*—gas pipeline to consumers; *17*—discharge pipe; *18*—nitrogen tank; *19*—nitrogen pipeline for forming protective screen; *20*—nitrogen pipeline for blowing out gas duct; *21*—water tank; *22*—pump for supplying water to scrubber and atomizer; *23*—hydraulic cyclone; *24*—settler; *25*—sludge pump; *26*—filter; *27*—pumps

Safe operation of the system is ensured by blowing the gas duct with nitrogen before supplying oxygen and after cutting off the oxygen supply, and also by pumping nitrogen through the gas dust during 5-6 minutes at the beginning and at the end of oxygen blowing, i.e., during the period when the content of CO in the gases is low and that of oxygen is large, which may cause the formation of an explosive mixture. Because of a varying content of CO in the gases during the heat, it is considered possible to afterburn the gases and discharge them through the stack at the beginning and at the end of the blow period when the CO content of the gases is not high. The gases are fed to a gas holder only when the CO content is higher than 60 per cent, so that the time of gas utilization is not more than 65-70 per cent of the blow time. The temperature of the gases after cleaning is 32°C and the residual dust content, not more than 0.25 g/m^3.

An installation operating by the OG system with gas cleaning can be made substantially smaller, since the amount of gases in this case is roughly only three times that of the oxygen used in the heat, whereas when gases are removed with afterburning and heat utilization, their amount is 15-20 times that of the oxygen consumed and even 25 times greater when gases are removed with afterburning and without heat utilization. The usage of nitrogen for forming the sealing screen is 38 m^3 per ton steel. This nitrogen has no effect on the content of nitrogen in the steel. When the system operates without afterburning, there is no danger of corrosion in the gas duct, since the gas predominantly consists of carbon monoxide.

In the USSR, operational schemes of gas cleaning without afterburning and with the use of nitrogen screen have been developed for 50- and 250-ton converters. The gas stored in gas holders can be used for chemical synthesis or as fuel when mixed with blast-furnace, coke-oven or natural gas.

Coarse cleaning of converter gases is effected in hydraulic cyclones (scrubbers) or disintegrators, and fine cleaning in atomizing (Venturi) tubes with the use of cloth filters and electric filters. Wet cleaning consumes much electric energy. Gas cleaners of this system employ cyclones, centrifuges or Venturi tubes. Hydromechanical systems with disintegrators and cloth filters ensure the degree of gas cleaning of 98-99.3 per cent (Waagner-Biro system) or even 99.95 per cent when filters of synthetic cloth type Tergal are used. Felt or cloth filters can be employed at a gas temperature not above 80°C, orlon and dacron filters up to 140°C, and glass fibre filters up to 260°C.

The systems of gas cleaning by means of cloth filters are based on cooling converter gases down to a temperature at which these filters can operate without damage. A system of this type is shown in Fig. 75. Converter gases are first directed into the chimney and then into a heat accumulator resembling the Cowper blast heater of blast furnaces. The checkerwork of this accumulator absorbs the heat of the waste gases, their temperature being lowered here down to 120°C which allows the use of cloth filters in subsequent treatment of the gases.

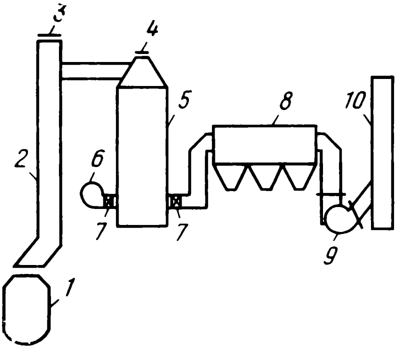


Fig. 75. Schematic diagram of converter gas cleaning with a heat accumulator and cloth filters

1—converter; *2*—chimney; *3*—manhole cover on the chimney; *4*—accumulator manhole cover; *5*—heat accumulator; *6*—fan; *7*—gate valves; *8*—filters; *9*—exhauster; *10*—stack

After passing through the filters, the dry and clean gases are fed into an exhauster and ejected through the stack into the atmosphere. Before starting the converter heat, the accumulator is cooled by passing through it cold atmospheric air blown by a powerful fan, restoring therewith its accumulating capacity. The cyclic operation of an oxygen converter makes it possible to use this system of gas cleaning. The efficiency of gas cleaning by cloth-filter plants may be as high as 99.95 per cent.

Hydromechanical systems with electric filters (for instance, the Waagner-Biro-Fest system) ensure the degree of gas cleaning of up to 99.8 per cent. The explosion-safe Pease-Anthony system, comprising a hydrocyclone and a Venturi tube, cleans converter gases to 98.8 per cent. The system is compact and operates with only a small inleakage of air used for afterburning. Diagrams of these gas-cleaning systems are shown in Fig. 76. Dry electrostatic dust-collecting filters can clean gases to 99.9 per cent and enable the use of dry dust containing up to 80 per cent of iron oxides; the drawback of these filters is that they are explosion-hazardous.

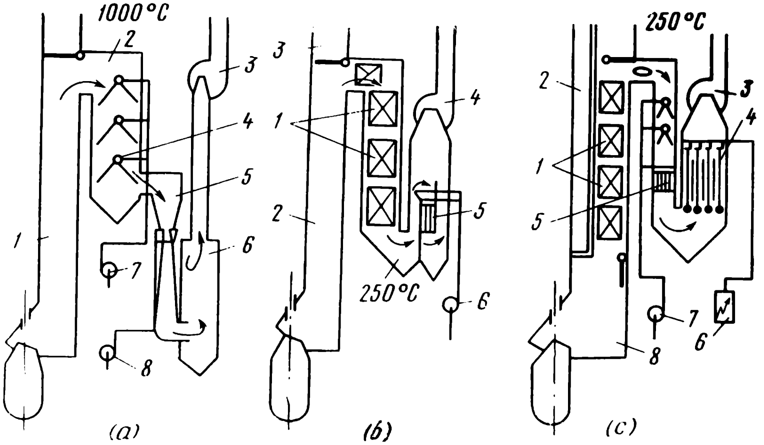


Fig. 76. Diagrams of gas cleaning

Pease-Anthony system: *1*—radiation boiler with refractory-lined surfaces; —scrubber; *3*—exhaust fan; *4*—scrubber nozzles; *5*—Venturi tube; *6*—cyclone; —scrubber nozzle pump; *8*—pump for feading water to scrubber; *b*—Waagner-Biro hydromechanical system: *1*—convective surfaces; *2*—radiation surfaces; stack; *4*—exhaust fan; *5*—hydraulic cleaning (filter); *6*—water-spraying pump; Waagner-Biro-Fest system: *1*—convective surfaces of waste-heat boiler; vacuum chamber; *3*—exhaust fan; *4*—electric filter; *5*—hydraluic cleaning filter; *6*—high-pressure generators; *7*—water pump; *8*—radiation surface

The standard design of an oxygen converter shop with 100-130-ton converters developed in the USSR incorporates a gas cleaning system with gas afterburning and utilization of heat in waste-heat boilers. The temperature of the gases at the outlet from the ascending gas duct (chimney) varies between 850 and 950°C and at the outlet from the boiler, between 250 and 300°C. The KB-19 system is provided in its lower portion, into which the gases are fed, with a scrubber where gases are cooled by water jets down to 70-90°C. The gases from the scrubber are supplied into atomizing tubes where they are scrubbed with water to coalesce dust particles. The gases are then fed to an electric filter and ejected into the atmosphere.

With such a system of gas cleaning, the amount of gases formed depends on the degree of air inleakage into the chimney, which, in turn, is decided by the width of the gap between the chimney and converter neck, and also by the value of negative pressure in the system. Depending on these parameters, the amount of air sucked in together with converter gases is $(45\text{-}79)\cdot 10^3$ m^3/h and increases up to 100,000 m^3/h at the entry to the gas cleaning plant.

The chimney in the system described is an ascending gas duct (radiation heater) of a waste-heat boiler. It is formed from vertical screen tubes arranged at the walls of a rectangular duct. Steam-water mixture formed in the tubes is pumped from circulation pumps. During the intervals between blow cycles, coke-oven gas is fired in the chimney in order to maintain the temperature of gases at 400-600°C. The actual steam output of the boiler is 50 tons per hour. The degree of gas cleaning is 99 per cent when the system is made in the form of a rectangular chamber. A scrubber is mounted in the lower portion of the system and banks of atomizing tubes are installed above it. The gases are cooled by water ejected from nozzles.

As has been indicated earlier, closed systems of gas cleaning operating without gas afterburning in the chimney are becoming popular. With this method of removal of converter gases their volume reduces almost by a factor of three. For instance, in the oxygen converter shop of the Karagandinsky iron and steel works removal of gases from 250-ton converters is made via hermetically sealed ducts without gas afterburning in chimneys.

The dimensions of plants for wet cleaning of gases are smaller than those of plants for dry cleaning. In addition, such plants remove harmful impurities (nitrogen oxide, sulphur, etc.) from the gases together with dust. A disadvantage of wet gas cleaning is a higher corrosion wear of the elements of the system. The system of dry gas cleaning with electric filters is more expensive because of its large dimensions.

FURTHER IMPROVEMENT OF THE OXYGEN CONVERTER PROCESS

Pig iron is more expensive than scrap, because of which the problem of increasing the proportion of scrap in oxygen-converter charges is very urgent. Besides, with the expected gradual reduction of the open-hearth steelmaking the utilization of scrap and metallurgical rejects in industrially developed countries will become a problem of high importance.

In the ordinary oxygen-converter process the proportion of scrap is 15-28 per cent. In some shops, however, it is increased up to 35-40 per cent, which is achieved by preheating the scrap. For this purpose, the converter is provided with a long lance (up to 20 m) of a diameter of 0.5 m. The end piece of the lance is made in the form of concentric copper pipes for distributing the natural gas supplied. The heat power of the gas-oxygen lance for scrap heating in a converter is maintained at a level of $0.4\text{-}0.6 \cdot 10^6$ kcal/min, since with a further increase of the supply of gas and oxygen the noise generated by the lance becomes unbearable for the personnel.

Examples may be mentioned from modern practice when high-carbon steel was made with 35 per cent of preheated scrap in the charge and soft and medium-carbon steels, with 40 per cent of scrap. As has been found, it is not rational to heat up scrap during more than 20 minutes, since heating is accompanied by strong oxidation.

Besides, it has been found that, when scrap begins to melt at its surface during heating, the affinity of the oxygen supplied to burn the gaseous fuel is greater for iron of the scrap than for the components of the natural gas, which increases the consumption of fuel.

Other methods also exist, which make it possible to increase the proportion of scrap in charges. For the proportion of scrap in the charge to be increased without preheating, additional chemical elements, for instance, silicon carbide or calcium carbide, are introduced into the charge, which upon burning evolve a large amount of heat. It is assumed that an addition of 1 kg of silicon carbide allows the proportion of scrap in the charge to be increased by 7 kg.

When using heat-forming elements in converters, the vessel is first charged with dolomite lime to protect its bottom against direct action of iron oxides flowing down from the melting scrap. After charging, a lance is introduced into the converter and adjusted 150 mm from the scrap surface. Already in 15 seconds the lance is made to operate with the consumption of 140-120 m^3/min of natural gas and 260 m^3/min of oxygen. Silicon carbide is stored in flux bunkers and charged into converters above the scrap after the latter has been heated up. Pig iron is then poured to carry out the heat by the common process.

If scrap becomes strongly oxidized during heating, then vigorous reactions may occur in the vessel after pouring in pig iron; to prevent this, pig iron must be poured in more slowly. On the other hand, a low proportion of pig iron in the charge and a high oxidation of preheated scrap make it possible to reduce the blow time to 10-11 minutes. A result sometimes may be that the lime does not dissolve completely in the slag (which can be partially explained by a high amount of lime in the charge), and also that the scrap does not melt completely.

In such cases the heats must be made with one or more overblows, which may result in a low carbon content of steel (0.05 per cent), a reduction of the yield by 2-2.5 per cent, and an increased content of oxygen and nitrogen in the steel. In some heats the content of nitrogen reaches 0.012 per cent against 0.004-0.005 per cent in ordinary heats.

An analysis of melts with the use of 40 per cent scrap in the charges (more than 5000 melts) made at a works in the USA has shown that this method is quite applicable for making steel in converters. When making steels with a high carbon content, it is not recommended to increase the proportion of scrap above 35 per cent. With a normal content of silicon in pig iron and when making steels with a carbon content more than 0.10 per cent, it is possible only to preheat scrap and avoid adding silicon carbide.

As has been found from experiment, the productivity can be somewhat increased by adding silicon carbide for scrap heating, but this method of scrap heating is seven times as expensive as that of scrap heating by gas; expenses of fluxes also become greater.

At the works of the Pittsburgh Steel and Ford Motor Companies, scrap in converters is heated up by means of fuel oil-oxygen burners, while the Republic Steel Works employ calcium carbide in converter melts. As has been indicated earlier, the cost of the materials used for heating scrap with fuel is lower than that of using calcium carbide.

Silicon carbide is less dangerous in operation and storage than calcium carbide from the standpoint of safety engineering. When calcium carbide is employed, care must be taken to keep it dry to ensure against formation of acetylene.

Thus, the existing shops prefer to employ carbides (better silicon carbide) as fuel for heating the scrap in the charge, while new shops provide conditions for heating scrap with natural gas or fuel oil.

It should be noted, however, that chemical heat carriers (calcium and silicon carbides) have not found wide industrial application for increasing the proportion of scrap in converter charges because of their high cost which results in an increased cost of the steel made. They also reduce the life of converter lining because of the formation of aggressive slags; furthermore, storage of calcium carbide is linked with certain difficulties. The proportion of scrap in the charge should be chosen separately for each kind of steel to be produced. For instance, low-carbon steels intended for deep and very deep drawing must possess high non-ageing properties; it is then very important that the nitrogen content in the final steel be as low as possible. This, in turn, depends on the content of nitrogen in technical oxygen. As has been shown by experiments, the residual content of nitrogen in steel can be reduced substantially by increasing the rate of decarbonization, all other things being the same. For that reason steels of these grades must be made by using as much pig iron as possible and by adding iron ore, rather than scrap, as the main coolant.

This technology ensures a more active boiling and rather intense decarbonization of the metallic bath, a lower consumption of oxygen, and therefore lower residual concentrations of nitrogen in the metal.

Cases are known from the Japanese practice when steel for deep drawing was made by subjecting the pig iron to preliminary desulphurization, and in some works lime is blown together with oxygen in order to have less than 0.006 per cent P in the metal. For this grade of steel the problem of ageing is considered the principal one. The metal becomes non-ageing with 0.001-0.006 per cent of dissolved nitrogen contained in it. For that reason melts are preferably carried out without overblow and are finished with the carbon content not less than 0.05 per cent; the metal should not be tapped in a powerful jet.

The problem of increasing the productivity of converters is among the principal ones in the development of oxygen-converter steelmaking. As is known, the productivity of a steelmaking plant is inversely proportional to the duration of melt, i.e., the smaller the time of current standstills of a converter and also the larger the mass of a melt, the greater the productivity. Thus, an increased mass of the charge, high stability of the converter lining, rapid charging of scrap in one pass, and turning down the vessel at the specified carbon content (i.e., making the heat without overblow) are basic prerequisites for increasing the productivity of converters and converter shops as a whole.

SPLASHES AND SKULLS IN CONVERTER NECK

An important problem in reducing the time of current standstills is the removal of metal skulls from the neck of converters which are formed owing to metal splashing during the blow. Another problem is the reduction of the time required for repairs of the taphole. The existing methods of removing skull are far from being perfect. Formation of skulls in converter throats may be prevented by developing special kinds of refractory not liable to skulling.

The intensity and number of splashings can be reduced by using a multi-nozzle lance instead of a single-nozzle one. The application of multi-nozzle lances has reduced the formation of skulls and thus shortened the time required for repairs of the throat, i.e., resulted in an increase of productivity of converters.

THE ANNUAL NUMBER OF HEATS

A very important characteristic of a correct organization of work in a converter shop is the number of heats performed in a converter during a year. This parameter characterizes the stability of the lining, the duration of intervals between the heats, the rate of charging, the time spent for cleaning and preparation of the taphole, and also the splashing conditions. As is known, the number of heats made during a year in a large converter in Japan sometimes reaches 12,000-14,000, i.e., substantially higher than in the USA, where the best indices achieved are 10,000 heats per year.

In a three-converter shop, as a rule, two vessels are always in operation and the third is being repaired. The third converter is sometimes put rapidly into operation in cases of emergency stoppage of one of the operating converters, for instance, as a result of a strong skulling of the throat or because of the need of repairing the taphole. This is done in order not to reduce the productivity of the whole shop. A long utilization of the spare vessel is, however, inadvisable.

When low-carbon rimming steel is made, the tap-to-tap time is substantially smaller than for making killed steel with 0.25-0.60 per cent carbon or especially for making alloy steel which is produced with several turnings of the vessel. Thus, the number of heats and the life of a vessel depend on the kind of steel being produced in it. These factors must be taken into account when making up the schedule of operation and repairs of a vessel and when distributing the grades of steel to be produced between the converters.

Reduction in the time of charging scrap and pouring pig iron is of a rather high importance. The time for charging scrap is dependent not only on the organization of work in the converter shop, but also on the conditions of preparation of scrap before melting and on the available equipment for rapid charging of scrap in one pass. In shops with a good organization of work the charging of scrap and pouring of iron into 150-200-ton converters take only three to four minutes.

The time of blowing depends on the specified intensity of oxygen supply, which is linked with the adopted system of gas cleaning, the availability of oxygen and the throughput capacity of the gas-removing ducts. The blowing conditions for many modern converters are calculated for an average blowing intensity of 2.5-3.0 $m^3/t \cdot min$. The tap-to-tap time for a vessel of the indicated capacity is then 34 to 42 minutes.

At some works there is a trend to increase the intensity of blowing up to 4-5 $m^3/t \cdot min$, but this can hardly have any effect on the tap-to-tap time and the number of heats per year. Firstly, it must be kept in mind that a definite time is required to melt the scrap (especially large pieces) and to let the lime pass into the solution, which is linked with the heat capacity and conductivity of these materials. Secondly, the blow period usually takes only 33 per cent of the total time of the heat. For that reason more attention must be paid to reducing the time spent for auxiliary operations. The correct organization of work and labour discipline may give a better effect than an increase of the intensity of oxygen blowing.

Reduction of current standstills of converters may have a large effect on the number of heats during a year. In order to reduce standstills, the lining of vessels is made roughly 900 mm thick from tar-dolomite or magnesite brick, the slag zone and taphole being made of the same kind of brick, but with a higher content of MgO. The zone subjected to impacts of steel scrap and the throat are lined thicker. The taphole is sometimes made of electric-melted magnesite in the form of shaped tubes which have a very high stability.

The blowing conditions are also a factor of large importance. In Japan, oxygen converters are blown with oxygen under a pressure of 10-11 at in most cases, but when making carbon steels with stopping of the blow at a specified carbon content, the pressure is reduced to 8-9 at. The height of the lance above the bath is usually kept constant during the whole melt, except for melts conducted with stopping of the blow at a specified carbon content. The operational programme for such melts provides two periods of blowing with varying the height of the lance above the level of the quiet bath.

In shops with a good organization of work, special instructions are developed for making each kind of steel, in which the proportions of pig iron and scrap in the charge, the amount of lime, fluorspar, oxygen, the height of the lance above the bath and the final temperature of the metal are accurately specified. A day before the beginning of a shift, the programme of production for the shift, the grade of steel to be made, the duration of heats and their sequence for all grades of steel for each converter are accurately prescribed. The height of the lance above the bath is allowed to be changed only in cases when the course of the process deviates from the normal run or when splashings are very strong. All workers must be acquainted with the instructions in due time.

When making soft grades of steel, the heat can be stopped at a specified carbon content comparatively easily. The problem becomes more complicated when carbon steels are produced with turning the vessel at a given carbon content. In the Soviet and foreign practice, it is allowed, when needed, to carbonize the metal in the ladle up to 0.02-0.05 per cent C, and even to 0.1 per cent C when making less critical grades of steel. The problem of stopping the heat at a specified carbon content and a given temperature can be solved more easily by using electronic computers for heat control. A problem of further progress in the control of the converter process is the development of a dynamic system of control and further improvement of measuring instruments with the aim of developing a closed system of process control.

Chapter Twelve

STEELMAKING IN OPEN-HEARTH FURNACES

With the rapid advance of iron and steelmaking the problem arose of obtaining various grades of steel in large quantities, a problem that could not be solved by the acid Bessemer and basic Bessemer (Thomas) processes. Large stocks of scrap accumulated in the industry, and its efficient utilization and the employment of pig iron unsuitable for converters became urgent problems.

The idea, suggested by Réaumur in 1722, of converting soft iron into steel by immersing it in molten pig iron, and then of producing steel by melting scrap and pig iron on the hearth of a reverberatory furnace, was the object of persistent research by Emile and Pierre Martin from 1840 to 1865 in Sireil (France). Only after they adopted Siemens' proposal (1856) for recovering the heat of exhaust gases for heating the fuel and the air supplied for combustion, did the Martins succeed in their undertaking.

In Siemens' furnace, the regenerators (Fig. 77) were filled with a checkerwork of refractory brick, made in the form of cells through which the combustion products from the reaction chamber were passed. By accumulating some of the heat of the waste gases, the checkers were heated to a high temperature. After a certain interval (10 or 12 minutes) the valves were reversed and the combustion products directed into a second pair of regenerators located at the opposite end of the furnace, while the hot checkers of the first pair were now used to heat the air and gaseous fuel before feeding them into the reaction chamber. Thus it became possible to raise the temperature in the reaction chamber to a level sufficient to melt a charge composed of pig iron and steel scrap and even to overheat it 80-100°C above the liquidus point.

Regenerative furnaces of this type had two ports located symmetrically at the ends of the reaction chamber, both of which served to admit air and gas and draw off combustion products.

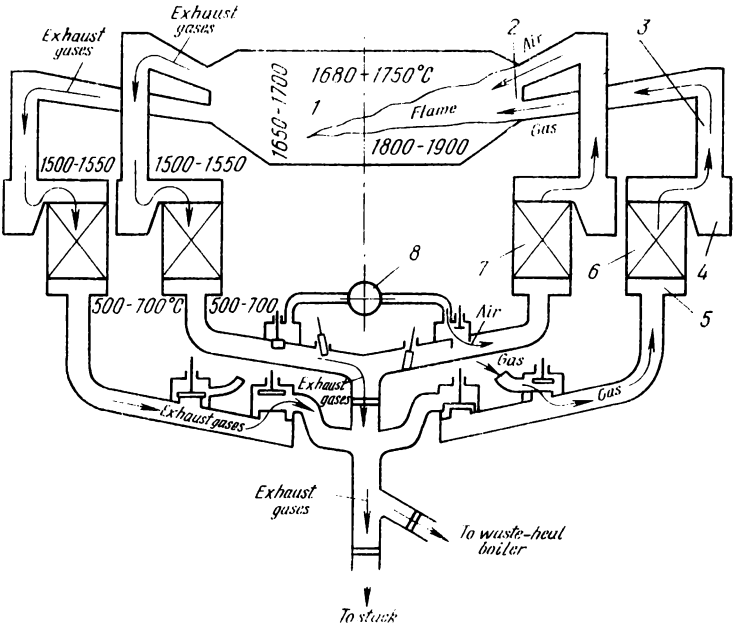


Fig. 77. Schematic diagram of an open-hearth furnace showing the temperatures in its elements

1—reaction chamber; *2*—ports; *3*—uptakes and downtakes; *4*—slag pocket; *5*—smoke flue; *6*—gas regenerator; *7*—air regenerator; *8*—blower

Later on, substantial improvements were made in the process itself and the construction of the furnaces. Thus, when the accumulated stock of scrap had been exhausted, a process was developed using a higher proportion of pig iron in the charge and employing iron ore to oxidize impurities.

In the first decades of its use the open-hearth process had already outstripped the Bessemer process in the volume of steel produced owing to its greater flexibility and adaptability to any scale of production, ease of control, less critical requirements placed on charging materials, and the possibility of producing both carbon and alloy steels. It was also employed for converting high-phosphorous pig iron in tilting-type units. Thus both acid and basic open-hearth furnaces were in use.

THE DEVELOPMENT OF OPEN-HEARTH STEELMAKING IN RUSSIA

The first Russian open-hearth furnace, of 2.5 ton capacity, was fired at the Sormovo works (now the Krasnoe Sormovo works) in February 1870. This furnace, built by A.A. Iznoskov and N.N. Kuznetsov, was of a more advanced design than the first ones built in France and the USA.

The technical and economic characteristics of open-hearth steelmaking, in particular labour productivity, improve with furnace size. Furnaces of large capacity (200, 300, 400 and 600 tons) are widely employed in the USSR, and more recently very large ones of a 900-ton capacity have been put into operation. More than 50 per cent of the total amount of steel produced by the open-hearth process are now made in furnaces of a size of 400-600 tons.

The production of open-hearth steel in this country continuously increases, but its percentage to the total production of steel begins to fall because of the accelerated growth of steel production in oxygen-blown Bessemer converters.

REFRACTORIES FOR OPEN-HEARTH FURNACES

A wide variety of types and grades of refractories is used to line open-hearth furnaces. The main requirements to be met by refractories are as follows:

(1) high refractoriness, enabling the furnace to be run at temperatures up to 1750-1800°C;

(2) chemical stability in contact with slag, metal, and gases; the eroding action of slags depends both on their chemical composition and physical state; the lining of

a furnace is damaged by the melting dust, the main components of which are iron oxides; the amount of dust in gases reaches 2 g/m^3 and is even higher if the bath is blown with oxygen;

(3) appropriate mechanical strength at high temperatures;

(4) stability with temperature changes, for the temperature of the lining varies sharply; thermal spalling is a result of mechanical stresses in the lining caused either by thermal expansion or by polymorphic transformations.

Refractories can be classified according to their chemical properties as:

(a) acid, i.e., those with distinct acid properties (silica brick, quartzite, etc.);

(b) basic, i.e., those with basic properties (magnesite brick, magnezite powder, magnesite-chromite brick with a high content of MgO, dolomite, etc.); and

(c) inert, i.e., those with the properties of amphoteric oxides (fireclay brick, chromite brick, chromites, fireclays, etc.).

Silica (Dinas) brick and semi-acid refractories. The main component of silica, SiO_2, has a low fusion point (1710 °C), but, since it retains its stability under load almost to the fusion point and has good chemical stability even at high concentrations of Fe_2O_3, it is a good refractory material.

In making silica brick, it has to be taken into account that quartz undergoes structural transformations (rearrangement of its crystal lattice) twice when heated to high temperatures, because three different modifications (quartz, tridymite, and cristobalite) are found in the natural mineral.

The transformation points of the stable modifications of quartz are as follows:

α-quartz $\rightleftarrows$ β-quartz	575 °C
β-quartz $\rightleftarrows$ β-tridymite	870 °C
β-tridymite $\rightleftarrows$ β-cristobalite	1470 °C
β-cristobalite $\rightleftarrows$ β-vitreous silica	1710 °C

The transformations of quartz are accompanied with volume changes that affect the strength of a lining. Adding

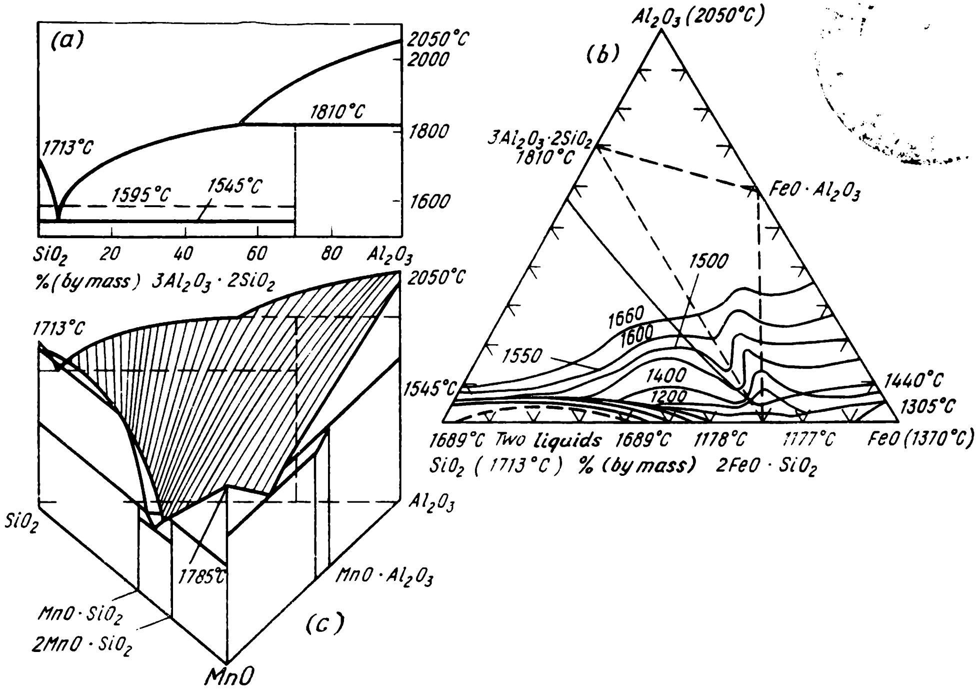


Fig. 78. Phase diagrams of various systems

a—SiO_2-Al_2O_3; *b*—SiO_2-FeO; *c*—SiO_2-Al_2O_3-MnO a small amount of lime (2-5 per cent) accelerates the transformation of quartz.

As will be seen from the phase diagram of the SiO_2-CaO system (see Fig. 13), an increase of CaO content to 48 per cent leads to the formation of fusible monocalcium silicate $CaO \cdot SiO_2$. The deleterious effect of FeO on the refractoriness of silica can be seen from the phase diagram of the SiO_2-FeO system (Fig. 78*b*). At 1750 °C, however, immiscible liquids are formed which remain in equilibrium. This property of silica brick makes it applicable for lining the reaction chambers of open-hearth furnaces, where the atmosphere is rich in vapours of iron oxides.

According to the Soviet State Standard (GOST), silica brick and silica articles must contain at least 93 per cent SiO_2 and not more than 1.5 per cent Al_2O_3 and 2.8 per cent CaO.

Fireclay brick. Fireclay (chamotte) brick, the main constituents of which are SiO_2 and Al_2O_3, stands up well the action of high temperatures (see Fig. 78). But this property is lost when it is in contact with FeO, as shown in the phase diagram of the SiO_2-Al_2O_3-FeO system (Fig. 79).

It will also be seen that the valuable property of pure silica (of withstanding the action of high concentrations of FeO through the formation of immiscible liquids) is lost with the addition of even a small percentage of Al_2O_3.

Because of the disruptive action of FeO, fireclay brick cannot be used to line furnace elements in contact with slag or the furnace atmosphere.

Fireclay can be used to line regenerators, in laying the lower courses of the hearth, and in appliances for tapping and teeming steel.

The chemical composition of fireclay brick varies within the following limits (in percentages): SiO_2 52-60, Al_2O_3 30-42, Fe_2O_3 1.5-2.5, CaO 0.5-1.5, MgO 0.1-1.0, and alkalis 1.0-2.0.

Magnesite brick. In the USSR, the starting material used to make magnesite brick is magnesite rock containing 98.03 per cent $MgCO_3$, 0.71 per cent $CaCO_3$, and 0.87 per cent $FeCO_3$.

Methods are now available for extracting MgO from sea water, in which it is present as $MgCl_2$ and $MgSO_4$. The melting point of pure MgO is 2800°C. When mixed with FeO, magnesium oxide forms a continuous series of solid solutions (Fig. 80). The fusion point remains very high

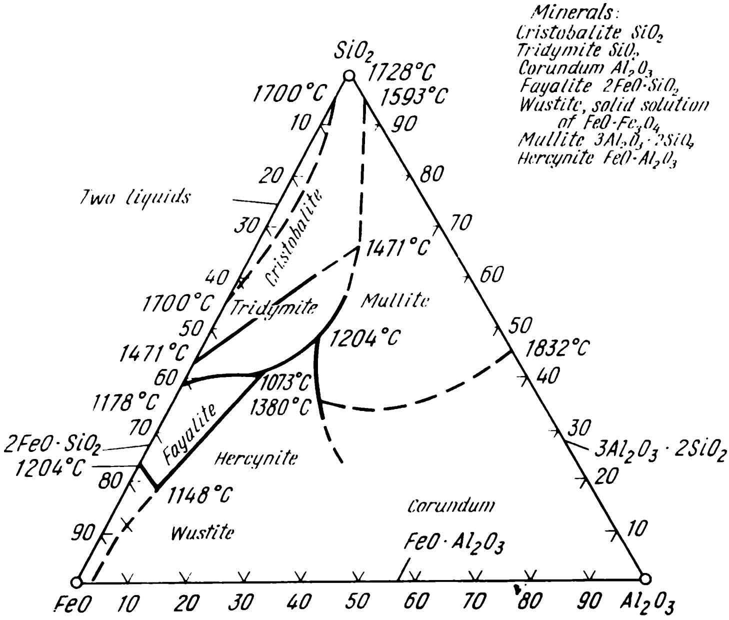


Fig. 79. Phase diagram of the ternary FeO-Al_2O_3-SiO_2 system

even when the solution contains as much as 50 per cent FeO, which is the reason why the magnesite hearth stands up well to the eroding action of slag.

Magnesite brick is employed to line the most critical parts of a furnace, e.g. the bottom, walls and ports of basic open hearths. Its disadvantages are its high thermal conductivity, high liability to spalling (i.e., a low thermal-shock resistance), and high thermal expansion.

Forsterite brick. The starting materials for making forsterite brick are magnesia-silicate rocks (dunite or olivinite) to which calcined magnesite is added. This brick, containing up to 85 per cent $2MgO \cdot SiO_2$ and 15 per cent $MgO \cdot Fe_2O_3$, is employed for laying the upper courses of regenerator checkerwork. According to the USSR technical specifications, the brick must contain at least 54 per cent MgO and not more than 32 per cent SiO_2. Forsterite brick possesses a high refractoriness (1830-1880°C) and high slag resistance and withstands well the erosion by melt dust. With regenerator checkerwork made of this brick, the temperature of the gases in the upper portion of the checkerwork must be at a level not higher than 1450°C. Dust deposits formed on the checkers must be periodically removed with compressed air (at a pressure of 5-7 at) or with water at a pressure of 12-14 at.

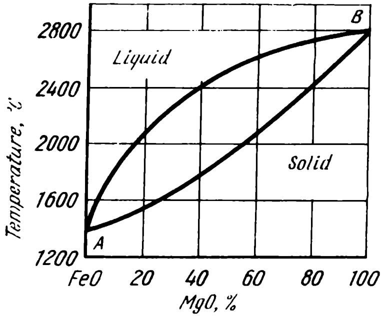


Fig. 80. Phase diagram of the MgO-FeO system

Chromite. Chromite ore in the pure form is a $FeO \cdot Cr_2O_3$ compound, which itself is a good refractory material. Its fusion point is 1780°C. Chromite is superior to silica and fireclay in its power to resist basic slags, and is less active with acid oxides. For that reason it can be considered a neutral refractory, and used in open-hearth furnaces as a separating material to isolate a basic lining from an acid one (for example, as an intermediate layer between courses of magnesite and silica brick).

Crushed chromite with an addition of fireclay is employed to fill gaps in furnace linings, to ram tapping holes, and for other purposes.

Chrome-magnesite refractories. As a refractory material, chromite is more often used mixed with magnesite, as a complex chrome-magnesite refractory, rather than in the pure form. For ramming furnace bottoms, magnesite powder is mixed with 5 to 10 per cent of chromite. The mixture obtained cakes or sinters well. In mixtures for making refractory bricks, the proportion of MgO may vary from 80 to 20 per cent, and that of chromite, from 20 to 80 per cent, respectively. In the USSR, magnesite-chromite brick (i.e., brick containing more magnesite than chromite) has found wide application, but in other countries mixtures containing 70 per cent chromite and 30 per cent magnesite are usually employed.

Chrome-magnesite brick is a highly refractory, thermostable material useful for lining the main roof and elements of the upper structures of furnaces. The disadvantage of chromite and chrome-magnesite refractories is that their chromium always undergoes reduction in contact with the liquid bath and contaminates the metal, which is unacceptable when making certain grades of steel.

Heat-insulating materials. The raw materials most commonly employed for making heat-insulating brick are diatomite, or infusorial earth (a hydrated form of silica), fireclay, asbestos, and vermiculite (up to 900°C). Light-weight porous fireclay (chamotte) or kaolin bricks are effective insulators (up to a temperature of 1200°C).

Materials for burning-in acid hearths. The material used for burning-in (ramming) the working layer of an acid hearth usually contains three components, varying in proportion from layer to layer (Table 27).

Table 27

Composition of Mixtures for Burning-in Acid Hearths (percentages)

Layers	Sand	Fireclay	Acid slag
1-4	90	6	4
5-8	92	4	4
9-12	95	3	2
13-15	97	1	2
16-19	98	—	2
20-22	100	-	—

The sand used in the hearth must contain at least 95-96 per cent SiO_2, while the remaining 4-5 per cent of admixtures must have a specified chemical composition, since their role is quite important. They act as mineralizers during the transformation of quartz into tridymite and cristobalite and thus facilitate sintering of the sand.

Ramming of the hearth, which used to be extensively employed, was later replaced by burning-in. Let us take, as an example, the method of making the hearth developed at the Urals Heavy Engineering Works using quartz (97.42% SiO_2, 0.22% Fe_2O_3, 1.24% Al_2O_3, 0.08% CaO, 0.14% MgO, and 0.42% calcination loss), clean quartz sand with at least 95.96 per cent SiO_2 and a minimum content of alkali earths, and return slag of the acid process ground to a grain size of 1-3 mm.

When the lining of the reaction chamber and regenerators has been heated sufficiently, the hearth is covered with a layer of ground acid open-hearth slag in order to slag the lining of the bath until it is completely impregnated. Excess molten slag is then removed through the taphole.

The next operation is to build up 24 successive separate layers of the refractory mixture, spread evenly over the hearth. The composition of the individual layers is gradually altered, as shown in Table 28, and each layer is burnt in for 3.0 to 3.5 hours.

Table 28

Composition of Mixtures for Burning-in Separate Layers of the Hearth

Layer No.	Composition (per cent)		
	quartz	sand	slag
1 and 2	50	50	—
3-15	45	45	10
16-20	25	65	10
21	—	94	6
22-24	—	100	—

After burning-in of the last three layers (consisting of pure sand), the hearth and banks are slagged for two or three hours until a pool of excess slag forms that is not absorbed by the hearth.

In Great Britain wide use is made of rammed hearths prepared from a 6 : 1 mixture of ganister and fireclay. The composition of the materials used is given in Table 29.

Table 29

Chemical Composition of Materials for Ramming the Hearth (percentages)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkalis
Ganister	95.32	1.23	0.86	traces	traces	traces
Fireclay	65.47	30.15	2.85	0.70	0.40	0.31

The disadvantage of a rammed hearth made in a cold furnace is that it swells and forms fissures when rapidly heated. The tendency of the quartz layers of a hearth to expand on heating is explained by the transformation of the quartz into tridymite and cristobalite, which have a lower density (the density of quartz being 2.65, of tridymite 2.32, and of cristobalite 2.35).

When properly laid, an acid hearth can last for eight years or longer, but it requires more skill and labour to maintain than a basic hearth and, besides, needs repair more frequently. The upper layers must be renewed periodically since iron oxides gradually diffuse through them, transforming the quartz into cristobalite.

The tendency of an acid hearth to undergo transformation and lose its valuable acid properties makes it necessary in practice to renew the upper layer by adding sand after each tapping.

The effect of the condition of the hearth on the quality of the steel produced in the acid open-hearth process is as important as that of the slag.

It is of interest to note that the same transformations occur in the silica of the furnace as in the acid hearth.

Materials for burning in (ramming) basic hearths. In this case burning-in is made with dolomite (or magnesium limestone), the chemical composition of which may be expressed by the formula $CaCO_3 \cdot MgCO_3$. It is quite a common rock containing 30.45 per cent CaO, 21.75 per cent MgO, and 47.80 per cent CO_2.

Raw dolomite should contain not less than 19 per cent of its most important constituent, MgO, so as not to shorten the life of the hearth. Admixtures must not exceed 7 per cent, but the presence of Fe_2O_3, SiO_2, and Al_2O_3 within

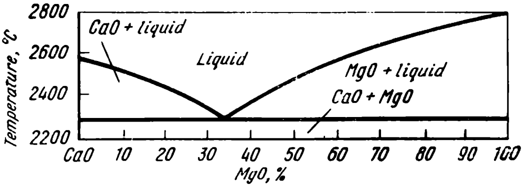


Fig. 81. Phase diagram of the CaO-MgO system

certain limits is even desirable in order to facilitate sintering. As will be seen from the phase diagram of the CaO-MgO

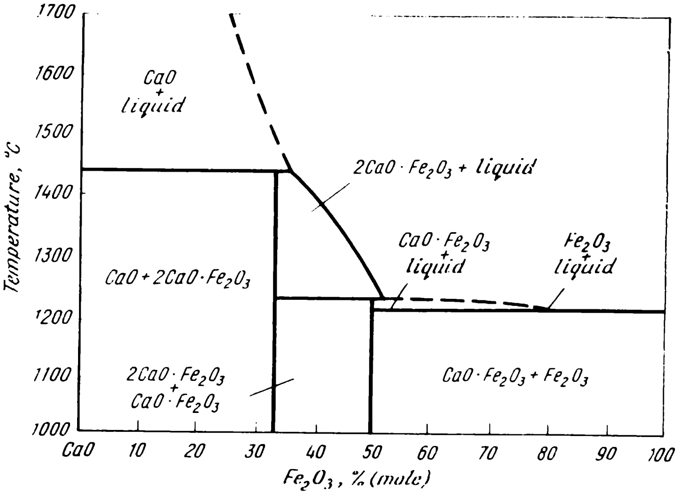


Fig. 82. Phase diagram of the CaO-Fe_2O_3 system

system (Fig. 81) mixtures of CaO and MgO are highly refractory.

It follows from the diagram of the CaO-Fe_2O_3 system (Fig. 82), however, that the formation of fusible compounds, calcium ferrites, can damage a dolomite hearth as a result of leaching of the lime.

Dolomite for fritting is always calcined completely, which raises its content of MgO to 35-38 per cent (Table 30).

Table 30

Chemical Composition of Soviet Dolomites (percentages)

Dolomite	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	H_2O	P_2O_5
Calcined	3.10	3.98	2.18	55.00	35.74	—	—	—
Raw	1.35	2.50	0.29	30.12	19.21	44.97	2.00	—
High-purity calcined	0.40	0.47	2.64	57.40	38.90	—	0.18	0.01
Double-calcined . .	0.40	0.50	7.40	52.40	38.68	—	—	0.01

Calcined dolomite tends to hydrate, so that it must be utilized as soon as possible.

Magnesite is also used for burning-in. Its main constituent is $MgCO_3$, which contains 47.62 per cent MgO and 52.38 per cent CO_2. There are also always impurities in natural magnesite (Table 31).

Table 31

Chemical Composition of Magnesites (percentages)

Magnesite	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	H_2O
Satka magnesite. .	0.20	0.07	0.54	0.40	46.90	51.73	0.16
	0.09	0.05	0.70	traces	47.46	51.70	
Ditto, calcined . .	1.0-2.5	2-4		1-2.5	92-90	—	—
Beloretsk magnesite	5.75	4.65		0.88	41.70	47.0	
Katav-Ivanovsk magnesite . . .	3.87	2.42	0.76	2.32	40.65	48.8	

The powdered magnesite of the Magnezit works has the following percentage composition: MgO 92-93.5, Fe_2O_3 1.5-3.0, Al_2O_3 0.9-3.0, CaO 1.0-2.5, and SiO_2 2.0-2.5. By the former method of burning in the hearth, some open-hearth slag or scale was added to calcined magnesite containing 92-90 per cent MgO.

The process of burning-in of basic hearths has been changed radically after successful experiments were carried out at the Serov iron and steel works. Instead of the earlier method of burning-in 14-15 layers, each 15-25 mm thick, the majority of open-hearth furnaces in the country are now burnt in with only one or two layers, each 150-250 mm thick. It has been found rational to use only ground magnesite, without any impregnation with slag or scale.

The new method saves much time: it requires only 5 to 7 hours to burn in a hearth instead of 70-140 hours spent earlier. The use of slag or scale for impregnation of magnesite powder has been rejected because magnesite powder contains, apart from periclase (MgO), about 8-10 per cent of other oxides (SiO_2, CaO, Fe_2O_3, FeO) which serve as the basis for the formation of a melt.

The scheme of diffusion of various oxides formed from slag impurities into periclase is such:

$$\underset{I}{MgO} + \underbrace{[SiO_2 + CaO + Fe_2O_3 + FeO + Al_2O_3]}_{II}$$

$$= \underbrace{[(CaSiO_4) + Mg(Al,\ Fe)_2O_4]}_{III}$$

$$+ \underbrace{[\text{solid solution of } (Mg,\ Fe)O + (Mg,\ Fe)Fe_2O_4]}_{IV}$$

Here: I = periclase (the main component of magnesite powder)

II = components present in magnesite powder which are in the slag phase at the temperature of burning-in (this phase participates in the process of formation of crystalline concretion)

III = components that bind the periclase

IV = periclase phase of burning-in

The diffusion of the slag phase formed from the impurities of magnesite powder into the periclase occurs slowly, which has been confirmed by actual data. For instance, not too thick a layer becomes monolithic in the new method of burning-in.

With the earlier methods of burning-in with thin layers and application of open-hearth slag in order to slag intermediate layers, the main components of the binder were $CaMgSiO_4$ (monticellite), $Ca_3MgSi_2O_8$ (merwinite), comparatively small amounts of Mg_2FeSiO_5 (olivines), 2(Mg, Ca,Fe)SiO_4 (ferromonticellite), Ca(Fe,Al)$_2$O$_4$ (alumoferrites), and still smaller amounts of spinels $MgO \cdot Al_2O_3$ and forsterite Mg_2SiO_4. With modern methods of burning-in, using the charge with 12 per cent of scale, the binder mainly contains calcium orthosilicate $CaSiO_4$ (which is more refractory than monticellite), *R*O-phase (Mg, Fe)O, and substantially smaller amounts of the above-mentioned minerals. For that reason some metallurgists consider it advisable to reduce the percentage of scale in the charge for burning-in.

One of the progressive trends in improving the stability of hearths is to ram a thick working layer of magnesite powder by using special vibromachines and pneumatic rammers, instead of burning-in.

EFFECT OF REFRACTORIES ON THE OPEN-HEARTH PROCESS

The roof of basic open-hearth furnaces is sometimes made from silica brick which participates in the formation of slag. Erosion of the silica brick by iron oxide vapours leads to thinning of the roof and walls by several millimetres per heat. The action of iron vapours is supplemented by the eroding action of lime, which settles as dust on the roof when the furnace is charged.

The destructive action of iron oxides on the silica lining is increased when the bath is oxidized with oxygen. A rough estimate is that the average loss of refractories in this way can be taken close to 0.2 per cent of the mass of the metal in the melt.

Silica of the lining runs down to the slag, thus reducing the basicity of slag, and makes it necessary to add lime. The materials of the hearth of a furnace also play an appreciable part in slag formation. The consumption of dolomite is usually 2.5-3.0 per cent of the mass of metal. Dolomite enriches the slag with calcium oxide and magnesium oxide. A magnesite hearth is much more durable than a dolomite one. Loss of magnesite from magnesite hearths is 0.7 per cent, and from magnesite-chromite roofs 0.15-0.10 per cent of the mass of the metal.

CHARGE MATERIALS

Fluxes. Limestone or its burnt product, *lime*, is used as a flux in both the acid and the basic process. Its harmful admixtures are silicon dioxide and sulphur. Silicon dioxide reduces the amount of free CaO in the flux, thus uselessly increasing the amount of the slag. The sulphur content of limestone, however, appreciably affects that of the metal, since it amounts to 10-30 per cent of the total sulphur introduced into a furnace with the charge. For that reason it is not advisable to use limestone containing more than 0.05-0.08 per cent of sulphur.

The limestone in the charge also serves as a good means for agitating the bath, since it evolves gaseous CO_2. This lime boiling improves heat-transfer conditions and accelerates refining through the oxygen of the CO_2.

Table 32 gives the composition of limestones of the Elenovsky deposit suitable for steelmaking.

Table 32

Composition of Limestones (percentages)

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	SO_2	Calcination loss
1	2.00	0.09	0.27	53.50	0.70	0.01	0.24	42.85
2	0.62	0.16	0.22	54.26	0.66	0.018	0.20	43.46

In the period of metal refining it is advisable to use lumped lime with lumps 60 to 120 mm in size, containing 86-90 per cent CaO, 2-3 per cent SiO_2, 1-3 per cent MgO, and not more than 0.08 per cent S, i.e., soft-burnt lime of white colour with sufficient porosity (1.7 g/cm^3).

Fluorspar (90-95 per cent CaF_2 and 3-9 per cent SiO_2)* is used to fluidize excessively thick slags. Its fluidizing action on the slag is accompanied by appreciable desulphurization of the bath. The desulphurizing effect of CaF_2 is explained by its activation of thick slag. Experience shows that this flux has a destructive effect on silica lining, caused by the reaction of CaF_2 and water vapour in the furnace atmosphere:

$$CaF_2 + H_2O \rightarrow CaO + 2HF$$

and the action of the resultant HF on the SiO_2 of the lining:

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4$$

The formation of SiF_4 is detected by the appearance of a thick white smoke from the stack and of a milky mist in the reaction chamber.

Bauxites are widely used in basic open-hearth steelmaking to control the fluidity of slags. Their fluidizing action is linked with the fact that they raise the concentration of Al_2O_3 in the slag. But the intensity of their action is inferior to the action of the CaF_2. Bauxites contain 6-10 per cent SiO_2, 25-28 per cent Al_2O_3, 0.8-3.0 per cent TiO_2, the rest being iron oxides. Consumption of bauxite, in practice, is seldom above 0.5 per cent of the mass of the metallic charge.

Broken fireclay (chamotte) brick is also added to slag in the acid process (and sometimes in the basic one) in order to increase its fluidity.

Iron ore is the principal solid oxidizer in the open-hearth process. It is added to accelerate burning-out of the impurities of the charge and to promote the dissolution of lime.

Analysis of certain iron ores employed in the open-hearth process is given in Table 33.

The silicon dioxide introduced with ore requires an increased input of lime, so that the amount of slag increases. For that reason the SiO_2 content of the ore should not exceed certain limits. Lump ore with a small amount of fines and of high density should be used for it to sink rapidly

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* Fluorspar with streaks of pyrite must be sorted out since pyrite contains sulphur. Fluorspar for steelmaking should not contain more than 1.5 per cent sulphur.

Table 33

Analysis of Selected Iron Ores (percentages)

Ore	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	MnO	Mn	P_2O_5	CO_2	S	H_2O	Calcination loss
A	62.25	7.80	1.00	0.18	0.05	—	0.16	0.035	—	—	—	1.80
B	86.74	2.39	1.99	1.21	0.21	1.99	—	0.009	0.38	0.034	4.42	—
C	87.57	5.90	3.15	0.80	0.69	—	0.08	0.064	—	0.021	—	3.15

in the slag. Violent splashing of metal and slag is possible if a furnace is charged with fine moist ore.

Another oxidizer, though seldom used, is scale (roll mill or forge). It is composed mainly of Fe_3O_4. The rough composition of scale is: 70.50% Fe, 2.50% SiO_2, 1.0% MnO, 0.04% P, and 0.02% S.

Scale is of low density and dissolves rapidly in slag before reaching the metal bath, and so is inferior to iron ore in its oxidizing action.

Iron ore can be partly replaced in the charge by manganese ore when the need arises to add manganese to the metal through the slag.

The composition of manganese ores employed in Soviet practice is given in Table 34.

Table 34

Chemical Composition of Manganese Ores (percentages)

SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	MnO_2	P_2O_5	Calcination loss
			Deposit I				
6.67	2.14	0.87	0.24	0.03	86.20	0.37	3.48
			Deposit II				
8.11	1.31	3.03	1.46	2.47	78.98	0.45	4.19

Ore fines in the form of briquettes and agglomerates are finding wide application in open-hearth furnaces. Fluxed agglomerate (41.7 per cent Fe, 9.0 per cent FeO, 34 per cent CaO, and 5.2 per cent SiO_2) has been tested in the conversion of high-phosphorous pig iron; this made it possible to exclude lime completely from the charge. The substantial amount of FeO, however, lowers its oxidizing power. Limestone-ore briquettes containing 37 per cent Fe, 24 per cent CaO, and 4 per cent SiO_2 were also tested in practice.

Scrap. Steel scrap to be charged in open-hearth furnaces must not be contaminated with sand, cement, sulphur, lead, zinc, tin, and enamels.

The lowest grade of scrap is light tin-plated and galvanized iron. The zinc coating of the latter evaporates on melting and settles as zinc oxide on the lining of the furnace and regenerators and on the fire tubes of waste-heat boilers and thus damages them.

Tin causes red-shortness in steel. Only with difficulty is it oxidized and removed with the slag. When lead gets into a furnace with the charge, it melts rapidly because of its low melting point, accumulates at the bottom because of its high density, penetrates the finest fissures in the hearth, and may even leak through the hearth. Cases of metal break-out through the hearth are linked with this property of lead.

Lightweight scrap includes steel turnings, sheet trimmings, etc. When a high proportion of scrap is used, charging is retarded and furnace productivity therefore is reduced; but this drawback can be eliminated by compressing the scrap in baling presses, which greatly improves charging conditions. Only fresh nonrusted turnings should be used in the charge (so that the bath is not overoxidized and saturated with gases), preferably in briquetted form. Large-size scrap is cut by shears or broken into pieces by means of a ram engine.

Steel scrap must be carefully graded. Thus, scrap of high-sulphur free-cutting steels must be carefully sorted out so as not to charge too much sulphur when making quality steels.

Pig iron. The main part of the charge of open-hearth furnaces is pig iron. At integrated iron and steel works, as a rule, liquid pig iron is charged into open-hearth furnaces. The steelmaking shop has a mixer to accumulate and mix the pig iron coming from the blast furnace shop.

In new shops, large-size mixer ladles have found use in recent years instead of stationary mixers. Liquid iron, before being charged into furnaces, is sometimes treated with caustic soda or lime and aluminium powder in order to desulphurize it; calcium carbide, magnesium, and other materials may also be used.

In steelworks without their own blast furnaces, pig iron is delivered in solid state, in pigs, which are charged into the furnaces. However, it is sometimes economical to remelt the pigs in cupolas prior to charging them into open-hearth furnaces.

When liquid iron is used in the pig-and-scrap process, it should not be introduced until after the charge materials have been heated to a temperature higher than its melting point so as to avoid chilling of the charge.

Pig iron must meet certain specifications. High-quality pig iron for the acid process is now produced in coke-fired blast furnaces with a sulphur and phosphorus content as low as in irons produced in charcoal-fired furnaces. For instance, the content of phosphorus in pig irons of various contents of silicon and manganese may vary from 0.02 to 0.06 per cent, and that of sulphur, from 0.015 to 0.025 per cent. Conversion iron for the basic open-hearth process (grades M1 and M2) may contain 0.75-1.25 per cent Si, 1.0-1.75 per cent Mn, 0.15-0.30 per cent P, and 0.03-0.07 per cent S, depending on its category, class, and group.

THE ROLE OF INDIVIDUAL ELEMENTS OF PIG IRON IN OPEN-HEARTH STEELMAKING

The carbon content of iron is affected by the level of the other components, it being increased by the effect of manganese, chromium, vanadium, and titanium which form carbides and reduced by silicon, phosphorus, and sulphur.

The nature and efficiency of the open-hearth process are very strongly affected by the phosphorus content of pig iron. In the acid process, in which it is impossible to remove phosphorus from the metal, the phosphorus content of pig iron must be kept to a minimum; and it is only when the pig iron accounts for just 20 or 30 per cent

Chemical Composition of

Ferro-alloy	Grade	Mn	C	Si	P
Ferro-manganese	Мн0	80.0	0.5	2.0	0.30
	Мн1	80.0	1.0	2.0	0.30
	Мн2	80.6	1.5	2.5	0.30
	Мн3	78.0	7.0	2.0	0.33
	Мн4	76.0	7.0	2.0	0.38
Ferro-silicon	Си90	0.5	—	87-95	0.04
	Си75	0.7	—	72-78	0.05
	Си45	0.8	—	45-50	0.05
Silico-manganese	Симн20	65	1.0	20.0	0.10
	Симн17	65	1.75	17.0-19.9	0.10
	Симн14	60	2.5	14.0-16.9	0.20
Silicon spiegel		18-24		9-13	0.20
Ferro-chrome	Хр0000	—	Under 0.06	1.5	0.06
	Хр000	—	0.07-0.10	1.5	0.06
	Хр00	—	0.11-0.15	1.5	0.06
	Хр0	—	0.16-0.25	2.0	0.06
	Хр01	—	0.26-0.50	2.0	0.06
	Хр1	—	0.51-1.0		0.10
	Хр2	—	1.1-2.0	2.5-3.0	0.10
	Хр3	—	2.1-4.0		0.10
	Хр4	—	4.1-6.5	2.0-5.0	0.07
	Хр6	—	6.6-8.0		0.07
Ferro-tungsten	В1	0.2	0.5	0.4	0.05
	В2	0.4	0.8	0.5	0.08
	В3	0.7	0.8	1.0	0.12

Table 35

Ferro-alloys (percentages)

Cr	W	Cu	S, not exceeding	Mo	Sb	V	Al	Ti	Sn, not exceeding	As, not exceeding
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
0.2	—	—	0.04	—	—	—	—	—	—	—
0.5	—	—	0.04	—	—	—	—	—	—	—
0.5	—	—	0.04	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
65	—	—	0.03	—	—	—	—	—	—	—
65	—	—	0.04	—	—	—	—	—	—	—
60	—	—	0.04	—	—	—	—	—	—	—
60	—	—	0.04	—	—	—	—	—	—	—
60	—	—	0.04	—	—	—	—	—	—	—
60	—	—	0.04	—	—	—	—	—	—	—
60	—	—	0.04	—	—	—	—	—	—	—
60	—		0.04	—	—	—	—	—	—	—
65	—	—	0.04		—	—	—	—	—	—
65	—	—	0.04	—	—	—	—	—	—	—
—	70	0.25	0.08	—	—	—	—	—	0.10	0.05
—	70	0.30	0.10	—	—	—	—	—	0.15	0.08
—	65	0.30	0.10	—	—	—	—	—	0.20	0.08

Ferro-alloy	Grade	Mn	C	Si	P
Ferro-molybdenum	Mo1	—	0.10	1.00	0.10
	Mo2	—	0.15	1.50	0.15
	Mo3	—	0.20	2.00	0.20
Ferro-vanadium	Вд1	—	0.75	2.00	0.10
	Вд2	—	0.75	3.00	0.20
	Вд3	-	1.00	3.00	0.25
Ferro-titanium	Ти1	—	0.20	3.50	0.05
	Ти2	—	0.20	5.00	0.08
	Ти3	—	0.20	6.00	0.10
Mirror iron	3-41	20.1-25	—	2.0	0.22
	3-42	15.1-20	—	2.0	0.22
	3-43	10-15	—	2.0	0.18
Blast-furnace ferro-silicon	Фс1 Фс2	3.00	1.2-1.5	9.0-13.0	0.15

of the total weight of the metallic charge that it is possible to produce acid steels containing not more than 0.015-0.020 per cent phosphorus.

In the basic process, it is possible to use pig iron of any phosphorus content, but the most advantageous for open-hearth furnaces is the content of phosphorus up to 0.2 per cent. With a phosphorus content above 1.5 per cent, pig iron still can efficiently be used in open-hearth furnaces since a very valuable by-product, phosphate slag, is produced.

Sulphur is the most undesirable element in the pig iron, since it can only be partially removed, even in the basic

Table 35 (continued)

Cr	W	Cu	S, not exceeding	Mo	Sb	V	Al	Ti	Sn, not exceeding	As, not exceeding
—	—	0.8	0.10	55	0.05	—	—	—	0.05	—
—	—	1.5	0.15	55	0.08	—	—	—	0.08	—
—	—	2.5	0.20	55	0.10	—	—	—	0.10	—
—	—	—	0.10	—	—	35	1.0	—	—	0.05
—	—	—	0.10	—	—	35	1.5	—	—	
—	—	—	0.15	—	—	35	2.0	—	—	
—	—	3.0	0.05	—		—	5.0	18	—	—
—	—	3.0	0.08	—	—	—	5.0	18	—	—
—		4.0	0.10	—	—	—	8.0	18	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.03	—	—	—	—	—	—	—
—	—	—	0.04	—	—	—	—	—		—

process. The sources of sulphur in the metal are pig iron, scrap, lime, and fluorspar.

Although silicon has a marked positive role in the heat balance of the open-hearth process, an excess of it in pig iron is undesirable, since the yield of steel can reduce through oxidation loss.

In modern steelmaking practice the content of silicon in pig iron is sometimes reduced by adding scale into the iron ladle or the launder of a blast furnace, by the method of prerefining, or by blowing pig iron in the ladle with oxygen.

Manganese is considered a useful element of pig iron. It acts as a desulphurizing agent in the mixer and promotes desulphurization of the bath. When using low-manganese pig irons, the lack of manganese in the bath is often compensated by enriching the slag with manganese ore, from which manganese is reduced and passes into the metal.

Ferro-alloys. All modern processes of making steel are finished by adding ferro-alloys with the object of deoxidizing the steel and alloying it. The compositions of the most common ferro-alloys are given in Table 35.

FUELS AND THEIR PROPERTIES

A fuel suitable for firing open-hearth furnaces must develop, on being burned, a calorimetric temperature of at least 2500°C; then, taking the pyrometric coefficient of 0.7 to account for external heat losses and the losses on the dissociation of combustion products, the actual temperature in the furnace will be 2500 × 0.7 = 1750°C, i.e., quite sufficient for the open-hearth process.

Open-hearth furnaces are fired by either gaseous or liquid fuels. In integrated works, they used to be fired with a mixture of coke-oven and blast-furnace gases preheated in the regenerators. Some furnaces operate on pure coke-oven gas. Blast-furnace gas cannot be used by itself because of its low calorific value (900-1100 kcal/m^3).

Natural gas has a high calorific value (7940-9000 kcal/m^3), and can be used cold in furnaces like coke-oven gas.

Liquid fuels, e.g. fuel oil and tar (10,200-8700 kcal/kg), are usually preheated (generally with steam) to facilitate atomization in the furnace burners.

As has been calculated, if powdered solid fuel is burnt with oxygen, air preheating can be dispensed with, i.e., the process can be carried out in a once-through furnace (without regenerators).

Typical compositions of the most common fuels used in steelmaking are given in Tables 36 and 37.

The requirements to be met by furnace fuels are as follows:

(1) they must ensure a high temperature in the furnace and provide a flame of the required radiance;

(2) for economical considerations, they should be a by-product of the same works or of a closely allied co-operating enterprise;

Table 36

Gaseous Fuels for Open-hearth Furnaces (percentages of volume)

Fuel	CO	CH_4	C_nH_m	H_2	CO_2	O_2	N_2
Producer gas from lignite	28.50	1.90	0.20	12.90	4.30	0.20	47.90
Coke-oven gas . .	6.5	25.6	2.5	54.5	2.0	0.6	8.3
Blast-furnace gas (coke-fired furnaces)	28.0	0.65	—	3.0	10.0	--	58.4
Blast-furnace gas (charcoal-fired furnaces) . . .	27.00	1.40	—	6.64	12.0	0.16	51.4
Natural gas . . .	—	92.40	4.2	—	0.3	—	2.8

Table 37

Liquid Fuels for Open-hearth Furnaces (percentages of mass)

Fuel	C	H_2	N_2	O_2	S	H_2O	Relative density
Tar	89.0	5.3	1.3	1.7	0.5	2.2	1.15
Fuel oil . . .	85.3	11.2	0.4	0.4	0.6	1.5	0.95

(3) they must be as free as possible of sulphur (as hydrogen sulphide, sulphur dioxide, or other compounds);

(4) the volume of combustion products per unit of heat produced must be as low as possible.

When fuels that give a non-luminous or only a slightly luminous flame (blast-furnace gas, natural gas, etc.) are employed, the first requirement is met by introducing a small amount of tar or fuel oil. The flame of natural gas can also be made luminous by carburization.

The carriers of sulphur in gases are SO_2 and H_2S. Sulphur mainly passes from gases to metal during the melting of scrap, which is accompanied with the formation of scale

($FeO \cdot Fe_2O_3$), apparently by the following reactions:

$$3Fe + SO_2 = FeS + 2FeO + Q$$

$$10FeO + SO_2 = FeS + 3Fe_3O_4 + Q$$

The ferrous sulphide formed is divided between the slag and liquid metal according to the distribution law. Thus, the presence of sulphur in furnace gases can appreciably affect the total sulphur content in the bath.

When high-quality steels are made, the sulphur content of the gas must not exceed 2.0 or 3.0 g/m^3.

It should also be taken into account that there is a partial settling of sulphur from the gases in the checkers. It has been observed that, when gases are heated in regenerators, they lose up to 20 or 30 per cent of their sulphur on their way to the reaction chamber.

The desulphurizing action of the checkers may be explained as follows. Settling of sulphur in the checkerwork is observed only after the regenerators have been in operation for a certain time. A definite amount of precipitated CaO and Fe_2O_3 is then always found on the surface of the brickwork, and when a gas containing H_2S is fed into regenerators, sulphides (FeS and CaS) are formed.

When the valves are reversed, flue gases of oxidizing nature are blown through the checkers, and the sulphides are converted into sulphates ($FeSO_4$ and $CaSO_4$); but these are immediately decomposed by the high temperature of the regenerators, for instance:

$$2CaSO_4 \rightleftarrows 2CaO + 2SO_2 + O_2$$

with the result that some of the sulphur is carried out into the stack.

Chapter Thirteen

ESSENTIALS OF THE OPEN-HEARTH PROCESS

The object of the open-hearth process is to convert the metallic charge into steel of a given grade. The composition of the metallic charge may vary from 100 per cent pig iron to 100 per cent steel scrap, and the pig iron may be charged in either the liquid or the solid state. To melt a solid charge and heat the metal to a temperature approximately 100°C above its melting point, and also to compensate for the heat losses during the idle run of the furnace, much external heat must be supplied to the furnace. In modern furnaces heat input may vary within broad limits, from 700 to 1500 kcal/kg of steel smelted, but it is substantially lower when the process is intensified by oxygen.

Atmospheric oxygen is supplied to a furnace in amounts exceeding those theoretically required for complete combustion of the fuel. This gives the gaseous phase an oxidizing character. Thus, the flow of gases contains oxidizing components (10.0-18.0 per cent CO_2 and 9.0-15.0 per cent H_2O) in addition to free atmospheric oxygen (0.5-0.8 per cent). These triatomic gases partly dissociate at the temperatures in the reaction chamber and give up their oxygen to the liquid bath.

The effect of the oxidizing gaseous phase on the metal begins from the very moment the furnace is charged. The impurities in the charge are oxidized along with the iron. Their non-volatile oxides pass into the slag being formed together with iron oxides and fluxes. The sand and dirt brought in with the pig iron and scrap, the refractories, and the products of oxidation of the lining and hearth are also involved in the formation of slag.

THE GAS-SLAG-METAL SYSTEM

There is a steep permanent pressure gradient of oxygen between the gaseous and metal phases in the reaction chamber. With complete combustion, oxygen pressure above the bath is hardly below 10^{-2} kg/cm^2 on average, which is slightly lower than the dissociation pressure of pure Fe_3O_4 at 1600°C, but much higher than that of the FeO that saturates pure iron (about 10^{-8} kg/cm^2 and even 10^{-9} to 10^{-10} kg/cm^2 when the bath contains some carbon). Hence it follows that the difference in oxygen pressure between the gaseous and the metal phase may be as much as 10^{-8} kg/cm^2, which provides conditions for a continuous flow of oxygen through the slag from the gaseous phase into the metal.

The approach to equilibrium in the gas-slag-metal system depends on the rate at which oxygen (as FeO*) passes from slag to metal in their contact zone:

$$(FeO) \rightleftarrows [FeO] \text{ or } (FeO) \rightarrow [Fe] + [O]$$

This rate in turn depends on whether the liquid masses in contact are in movement or still, and on the area of the contact surface. When there is intense mixing of metal and slag, very high reaction rates may be attained between the phases.

The main aim of the steelmaker is to provide slag conditions that will ensure a proper oxidation rate of impurities and ensure that the oxides of the elements undesirable in the steel are retained in the slag.

The composition and temperature of the metal after melting are a long way from those of the steel required. Melting is therefore followed by a period of refining, during which the bath is heated further and its constituents are oxidized.

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* Taken conditionally. Some metallurgists hold that oxygen dissolves in the metal in the form of FeO rather than in the atomic state, reasoning from the following: (1) the liquid phase appears at 1600°C even at extremely low oxygen pressures, and (2) the solubility of oxygen rises with temperature, which contradicts the law of solubility of gases. According to current views, iron and oxygen are present in the metal in ionic form. For the metal, iron oxide is usually considered to be present in atomic form [O].

SOURCES OF OXYGEN FOR OXIDATION OF IMPURITIES IN THE MOLTEN BATH

In the pig-and-scrap process oxygen consumption during the refining period does not exceed 3.5 per cent of the metallic charge; in the scrap-and-ore process it may be 8 per cent or higher. This explains why slag must have oxidizing properties, since the rate of the refining stage depends on them. Oxygen is supplied from the furnace atmosphere and from the oxides of the charge.

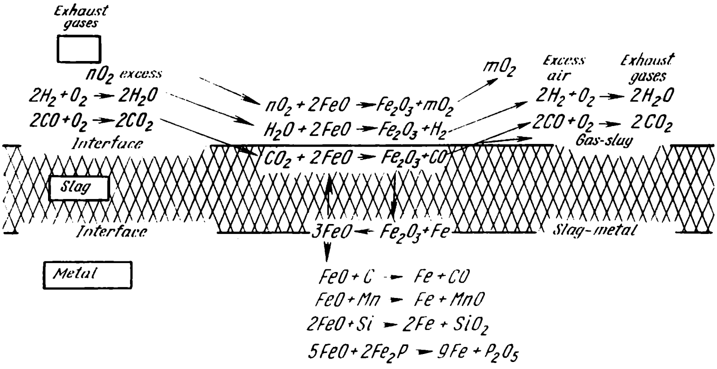

Fig. 83. Passage of oxygen from the gaseous phase into the bath

Slag becomes oxidizing just as it is formed through the accumulation of higher oxides of iron (Fe_2O_3, Fe_3O_4) that come from the scrap. Thus slag is an intermediate link in the oxidation process in the gas-slag-liquid metal system.

The process of oxygen transfer by slag is shown in Fig. 83; Fe_2O_3 is an oxide with a high dissociation pressure; it is converted into Fe_3O_4 at 1383°C with liberation of some of its oxygen:

$$2Fe_2O_3 \rightleftarrows 2Fe_3O_4 + {}^1/_2O_2$$

The gases in the reaction chamber always contain, apart from free oxygen, CO_2 and water vapours, H_2O, which also are oxidizers. With decomposition of limestone, CO_2 is formed, which plays the part of an oxidizer when passing through the metal into the furnace atmosphere.

The ferric oxide formed at the gas-slag interface diffuses through the slag and reacts with the liquid iron at the slag-metal interface, where it is reduced to FeO which passes into the slag, so that the concentration of Fe_2O_3 in the slag becomes minimal at the slag-metal interface. Thus a continuous cycle of oxidation of FeO to Fe_2O_3 occurs due to the gases moving above the slag surface. At the same time, through another reaction

$$Fe_2O_3 + Fe = 3FeO$$

the slag-metal interface is enriched in ferrous oxide.

Being soluble in both steel and slag, ferrous oxide FeO is distributed between them by the Nernst law. It should be noted, however, that this holds true only for the free ferrous oxide in the slag, i.e., the ferrous oxide not combined chemically. In accordance with the distribution law, enrichment of the slag with ferrous oxide causes oxygen to pass into the metal. It is this phenomenon that accounts for an exceptional role of ferrous oxide in the process of refining of the open-hearth bath. For instance, with a high percentage of liquid iron in the charge, much iron ore must be charged into the furnace for the oxygen of this ore to oxidize impurities of the metal. The iron of the reduced portion of the ore passes to the metal, thus increasing the yield of steel. In the oxidizing atmosphere of the reaction chamber, however, the reduction of ore cannot be complete, and usually comes to 90-92 per cent or even less.

OXYGEN CONSUMPTION PER HEAT

The pig-and-scrap process. The temperature to which the metal must be heated in the furnace before tapping depends on its chemical composition, in the first place on the content of carbon. For low-carbon steels this temperature is usually around 1600°C.

It may be roughly assumed for the pig-and-scrap process that the temperature of the bath must be raised by 300°C during the period from meltdown to tapping, which is mainly ensured by burning fuel in the reaction chamber.

In normal thermal conditions the amount of oxygen consumed in the pig-and-scrap process to oxidize impurities usually varies from 60 to 70 per cent of the total amount of oxygen consumed during the heat, of which about 70 per cent goes to oxidize carbon. The oxidation of carbon is the most important factor in the open-hearth process; the proper charge composition is therefore mainly determined by its concentration at the moment of meltdown.

In furnaces of high thermal capacity and advanced design, fired with high-grade fuel, the charge may contain a lower percentage of carbon than in furnaces of older design, or at the end of campaign or when fired with low-grade fuel.

The oxidation of carbon proceeds at a substantially lower rate in an acid furnace than in a basic one, so that its pig iron consumption is lower as a rule than that of the basic one.

The scrap-and-ore process. This version of the open-hearth process is employed in steel works where liquid iron is available directly from blast furnaces. The proportion of iron in this process is usually above 55 per cent of the metallic charge. The oxidation of impurities in the bath is accelerated by adding iron ore or scale. By yielding up their oxygen to bath impurities, the iron oxides of the ore are reduced to metallic iron and partly to ferrous oxide, thus enriching the slag with this oxide. Since the charge contains a large amount of iron ore (15-20 per cent of the mass of the metallic charge), the version of the open-hearth process using a high percentage of iron ore and liquid iron is termed scrap-and-ore or pig-and-ore process.

In this process, the role of the gaseous phase is substantially lower than in the pig-and-scrap process, since scrap is subjected to the action of the furnace atmosphere for a shorter time. It may be taken for calculations that the amount of oxygen supplied from the gaseous phase is 30 to 40 per cent of the total oxygen required for the heat.

REACTIONS OF OXIDATION AND REDUCTION OF IMPURITIES IN OPEN-HEARTH BATH

As with the Bessemer processes, the interaction between slag and metal in the open-hearth process obeys the laws of physical chemistry, but the conditions for attaining equilibrium are even more favourable here.

Experience shows that the distribution of most of the components (Mn, Cr, Si, P, and S) involved in the reactions between metal and slag is very close to equilibrium in certain conditions.

Oxidation and reduction of iron. When the metallic charge is melted in the furnace, its surface layers are oxidized into iron oxides by the following scheme: Fe → FeO, FeO → Fe_3O_4, and $Fe_3O_4 \rightarrow Fe_2O_3$. The impurities in the metal (C, Si, Mn and P) are also oxidized (to CO, SiO_2, MnO, and P_2O_5). Thus, a slag with a high concentration of iron oxides begins to form from the very start of the heat, i.e., during charging and melting. The ore participating in the formation of the slag in the scrap-and-ore process is responsible for the formation of highly ferruginous slags in the initial stage of the process.

As the molten bath is formed, it absorbs oxygen from the slag because the free FeO of the slag is distributed according to the distribution law between the slag and the metal. The passage of oxygen from slag to metal $(FeO) \rightleftarrows [FeO]$ is the most important moment in the process, on which the whole course of the melt depends.

The positive thermal effect of the reactions of formation of Fe_3O_4 and Fe_2O_3

$$3FeO + {}^1/_2O_2 \rightarrow Fe_3O_4; \quad \Delta H = -72{,}670 \text{ cal}$$

$$2FeO + {}^1/_2O_2 \rightarrow Fe_2O_3; \quad \Delta H = -68{,}050 \text{ cal}$$

allows us to infer that the lower the temperature during the melting of the charge, the higher will be the concentration of ferrous oxides in the slag. It would be wrong, however, to conclude that the metal is more saturated with oxygen, since the solubility of oxygen in metal falls with decreasing temperature, and its distribution between slag and metal is also dependent on temperature.

Oxidation and reduction of silicon. In a basic open-hearth silicon of the melt is almost completely oxidized when the temperature of the melt is still low. After melting its concentration in the bath is usually insignificant. The formation of SiO_2 by the reaction

$$[Si]^* + 2(FeO) \rightarrow 2Fe_l + (SiO_2); \quad \Delta H = -78{,}990 \text{ cal}$$

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* Conventional symbol; in fact silicon is dissolved in molten steel as a FeSi compound.

and of iron monosilicate by the reaction

$$(SiO_2) + 2(FeO) \rightarrow (FeO)_2 \cdot SiO_2; \quad \Delta H = -5\,900 \text{ cal}$$

is of prime importance for the formation of slag in the initial stage of the process and may play a certain part in its heat balance, depending on the silicon content of the charge.

The condition of equilibrium of the reaction of silicon with slag is expressed by the equation

$$\log K_{Si} = \log \frac{(a_{SiO_2})}{[\%\ Si]\,(a_{FeO})^2} = \frac{18,360}{T} - 6.68$$

The low activity of silica in the basic slag determines a rapid decrease of the concentration of silicon in the metal.

FeO is displaced from silicates by the stronger base CaO, as the latter dissolves in the slag:

$$(FeO)_2 \cdot SiO_2 + 2(CaO) = (CaO)_2 \cdot SiO_2 + 2(FeO); \quad \Delta H = -27,940 \text{ cal}$$

Thus stable calcium silicate is formed and FeO becomes a free component of the slag.

Since SiO_2 is in combined state in basic slags, the oxidation of silicon in basic processes should be considered practically irreversible, i.e., reduction of silicon from its oxides in the slag never occurs.

For acid processes the picture is quite different. The content of silicon in the bath does not fall below 0.02 per cent. Silica-saturated slags and the high-silica lining of the hearth create conditions favourable for the reverse reaction, in which endothermic reduction of silicon by iron occurs as the temperature of the bath rises:

$$2[FeO] + [Si] \rightleftharpoons SiO_2 + 2[Fe]$$

In the expression for the constant of the reaction

$$K = \frac{[SiO_2]}{[Si] \cdot [FeO]^2} \quad \text{or} \quad K = \frac{[SiO_2]}{[Si] \cdot [O]^2}$$

the concentration of SiO_2, which is practically insoluble in iron, may be taken as unity. Then

$$K = \frac{1}{[Si] \cdot [FeO]^2} \quad \text{or} \quad K'_{Si} = [Si] \cdot [FeO]^2 \ (\text{or } [Si] \cdot [O]^2)$$

The theoretically calculated constant for a temperature of 1600°C differs from the one determined experimentally:

theoretical . .	0.56×10^{-4}
experimental (1)	7.1×10^{-4}
experimental (2)	1.65×10^{-4}

The discrepancy may be explained by the difficulties encountered in experimental determination of the constant

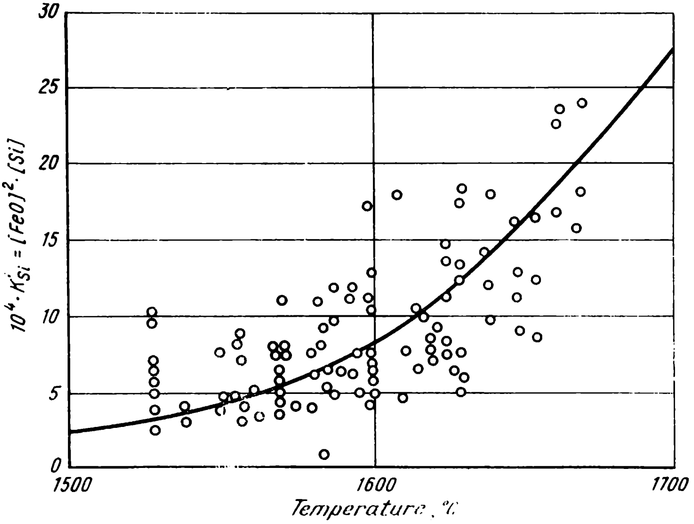

Fig. 84. Dependence of the equilibrium constant K'_{Si} on temperature

at very low concentrations of the elements, when the accuracy of measurements is no longer reliable.

As will be seen from the diagram in Fig. 84, the constant $[Si] \cdot [FeO]^2$ varies considerably with increasing temperature:

temperature, °C	1500	1600	1680
$K_{Si} \cdot 10^{-4}$	2.7	7.1	21.0

In the acid process, silicon can also be reduced by manganese, whose properties are similar to those of iron and whose oxide, MnO, is combined in similar compounds, as is FeO, with SiO_2 of the slag.

The role of manganese as a reducing agent cannot, however, be substantial in the acid process since its concentration in the bath is usually low; its noticeable effect is displayed only when it is added to deoxidize the bath.

With a hot run of the acid process, the reduction of silicon is always intensive, but it is still impossible to state with certainty whether silicon is directly reduced by carbon

$$(\mathrm{SiO_2}) + 2[\mathrm{C}] \rightarrow [\mathrm{Si}] + 2\{\mathrm{CO}\}$$

or the role of carbon is only indirect and the reduction of silicon is the result of the two simultaneous reactions:

$$\begin{array}{c} (\mathrm{SiO_2}) + 2[\mathrm{Fe}]_l \rightarrow [\mathrm{Si}] + 2(\mathrm{FeO}) \\ + \\ 2(\mathrm{FeO}) + 2[\mathrm{C}] \rightarrow 2[\mathrm{Fe}]_l + 2\{\mathrm{CO}\} \\ \hline (\mathrm{SiO_2}) + 2[\mathrm{C}] \rightarrow [\mathrm{Si}] + 2\{\mathrm{CO}\} \end{array}$$

The reduction of silicon by iron is only possible when the oxygen concentration in steel is negligible.

Oxidation and reduction of manganese. Manganese is readily oxidized in both the acid and basic processes, the exothermic reaction of manganese oxidation

$$[\mathrm{Mn}] + (\mathrm{FeO}) \rightarrow (\mathrm{MnO}) + [\mathrm{Fe}]; \quad \Delta H = -32{,}900 \text{ cal}$$

being more complete and intense in the acid furnace, since the reaction product MnO passes immediately and completely into a combined state (a silicate), except for the part that is present in the slag in a free state as a result of dissociation of the silicate.

It has now been shown that MnO is practically insoluble in steel. But its capacity to form fusible alloys with ferrous oxide, which are precipitated from the solution as slag, makes it possible to write the reaction of oxidation of manganese with the ferrous oxide dissolved in the metal as follows:

$$[\mathrm{Mn}] + [\mathrm{FeO}] \rightleftarrows (m\,\mathrm{MnO} \cdot n\,\mathrm{FeO}) + [\mathrm{Fe}]$$

In addition, since an oxidation reaction is also possible at the metal-slag interface and is an exothermic reaction, too, it may be written as follows:

$$[\mathrm{Mn}] + (\mathrm{FeO}) \rightleftarrows [\mathrm{Fe}] + (\mathrm{MnO})$$

The condition of equilibrium of the reaction of manganese with slag may be expressed by the equation

$$\log K_{\mathrm{Mn}} = \log \frac{(a_{\mathrm{MnO}})}{[\%\ \mathrm{Mn}]\,(a_{\mathrm{FeO}})} = \frac{6440}{T} - 2.95$$

It may be concluded from the data of practical experiments that the reaction of manganese oxidation readily attains equilibrium in the open-hearth furnace, after which the oxidation process gives way to reduction.

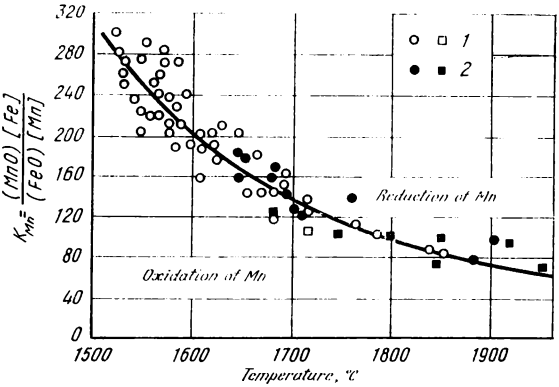

Fig. 85. Dependence of the equilibrium constant K_{Mn} on temperature
1 –Mn in metal; 2 –MnO in slag

Experimental study of the equilibrium constant* of this reaction for various melts

$$K_{\mathrm{Mn}} = \frac{(\mathrm{MnO})\,[\mathrm{Fe}]}{(\mathrm{FeO})\,[\mathrm{Mn}]}$$

shows that K_{Mn} decreases with rising temperature and, consequently, that the concentration of [Mn] in the metal increases (Fig. 85), from which it follows that the reaction of manganese reduction is indicative of a hot run, i.e., serves as a ‘pyrometer’ of the process.

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* The expression for the constant does not take into account the activity of the MnO and FeO in the slag, which may be taken as unity in basic slags of a basicity of 2.5 or higher.

Reversibility of the oxidation reaction of manganese is unlikely in the basic and acid processes. Nevertheless, reduction of manganese, which readily occurs in the basic furnace, is also observed in the acid furnace, usually simultaneously with silicon reduction.

Apart from iron, the reducing agent for the manganese is the carbon of the bath. The process may occur in one of the two ways: either through direct interaction between manganous oxide and carbon at the slag-metal interface

$$(MnO) + [C] \rightarrow [Mn] + \{CO\}$$

or, which is more likely, by two simultaneous reactions:

$$\begin{array}{c} (MnO) + [Fe] \rightarrow [Mn] + [FeO] \\ \underline{[FeO] + [C] \rightarrow [Fe] + \{CO\}} \\ \hline (MnO) + [C] \rightarrow [Mn] + \{CO\} \end{array}$$

The direct interaction of the carbon and the MnO of the slag can only proceed, however, at high concentrations of MnO and relatively low concentrations of FeO in the slag, and occurs less readily than the reduction of FeO, as may be seen by comparing the thermal effects of the reactions:

$$(MnO) + [C] \rightarrow [Mn] + \{CO\}; \quad \Delta H = 66{,}750 \text{ cal}$$

$$(FeO) + [C] \rightarrow [Fe] + \{CO\}; \quad \Delta \mathrm{H} = 34{,}460 \text{ cal}$$

Finally, in the acid process the silicon being reduced may act as a reducing agent for Mn:

$$(FeO) + [Mn] = [Fe] + (MnO)$$

$$(FeO) + {}^1/_2[Si] = [Fe] + {}^1/_2(SiO_2)$$

Denoting the constants of the reactions respectively by K_1 and K_2, we have

$$FeO \cdot Mn \cdot {}_1K = Fe \cdot MnO$$

$$FeO \cdot \sqrt{Si} \cdot K_2 = Fe \cdot \sqrt{SiO_2}$$

Eliminating Fe and FeO by division, we get

$$\sqrt{Si} = \frac{K_1 Mn}{K_2 MnO} \sqrt{SiO_2}$$

Since the concentration of SiO_2 in acid slags can be taken close to a constant value of 50 per cent, we may conclude that [$\sqrt{Si}$] varies proportionally with the Mn/MnO ratio, which has been confirmed by tests (Fig. 86).

By adding manganese ore to the charge and thus increasing the concentration of MnO in the slag and by raising the temperature, favourable conditions for the development of the manganese reduction reaction can be provided in the bath.

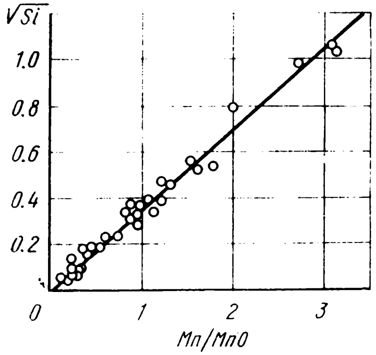


Fig. 86. Relationship between $\sqrt{Si}$ and [Mn] : (MnO) ratio

Oxidation and reduction of phosphorus. Phosphorus is usually considered a harmful impurity in steel and is used as an alloying additive only for certain grades of special steel.

Most of the phosphorus in the solid metal is in the form of the phosphides Fe_2P, Fe_3P, FeP, and FeP_2.

The phase diagram of the Fe-P system is not yet sufficiently studied. When examining the phenomena occurring in the molten bath it is assumed that all the phosphorus present is the phosphide Fe_2P. This is why the presentation of the process of dephosphorization is based here on the assumption that phosphorus is present in the bath as Fe_2P. The reaction of formation of this phosphide is

$$2Fe + P = Fe_2P; \quad \Delta H = -45{,}220 \text{ cal}$$

Dephosphorization begins already at low temperatures of the molten bath by the reaction (conventional symbols)

$$2[P] + 5(FeO) \rightleftarrows (P_2O_5) + 5[Fe]; \quad \Delta H = -47{,}850 \text{ kcal} \qquad (1)$$

or

$$2[Fe_2P] + 5(FeO) \rightleftarrows (P_2O_5) + 9[Fe] \qquad (2)$$

which reactions evolve heat when they proceed from the left to the right and bind the P_2O_5 formed into a stable compound in the slag, thus inhibiting the reverse reaction; P_2O_5 cannot exist in the free state since it is unstable at high temperatures. When stronger reducers of P_2O_5 are lacking in the bath, the role of reducing agent is played by carbon or iron:

$$P_2O_5 + 5C \rightarrow 2P + 5\{CO\}$$
$$P_2O_5 + 5Fe \rightleftarrows 2P + 5FeO$$

Iron phosphates $Fe_2O_3 \cdot P_2O_5$, $2Fe_2O_3 \cdot 3P_2O_5$, and $3FeO \cdot P_2O_5$ may also be formed in the bath, but they are rather unstable judging from the thermal effects of the reaction they are formed by. The most important of them is iron triphosphate which is formed by the reaction

$$3FeO + P_2O_5 = (FeO)_3P_2O_5; \quad \Delta H = -30{,}600 \text{ cal}$$

In the basic open-hearth process, the temperature conditions of the melt are insufficient for dephosphorization through the formation of iron triphosphate.

The unstable iron triphosphate is removed from the furnace by skimming off the initial ferruginous slags. The drawback of this method is a substantial loss of iron in the slag, but it is widely employed in the scrap-and-ore and the pig-and-scrap processes.

It may be taken that CaO plays the main part in the dephosphorization of open-hearth steels, provided that a certain FeO/CaO ratio is observed in the slag.

Of all the components of the basic slag, CaO forms the most stable compound with P_2O_5, as can be seen from the heats of formation of the compounds:

$$4(CaO) + (P_2O_5) = (CaO)_4P_2O_5; \quad \Delta H = -165{,}700 \text{ cal}$$
$$3(CaO) + (P_2O_5) = (CaO)_3P_2O_5; \quad \Delta H = -159{,}500 \text{ cal}$$
$$3(MgO) + (P_2O_5) = (MgO)_3P_2O_5; \quad \Delta H = -114{,}900 \text{ cal}$$
$$3(MnO) + (P_2O_5) = (MnO)_3P_2O_5; \quad \Delta H = -87{,}500 \text{ cal}$$
$$3(FeO) + (P_2O_5) = (FeO)_3P_2O_5; \quad \Delta H = -30{,}600 \text{ cal}$$

The strong bond between CaO and P_2O_5 can be destroyed by SiO_2 present in the free state:

$$(CaO)_4P_2O_5 + 2(SiO_2) = 2\,(CaO)_2 \cdot SiO_2 + (P_2O_5)$$

so that an indispensable condition for effective dephosphorization is that there should be sufficient CaO in the slag to ensure the formation of $(CaO)_4P_2O_5$ and $(CaO)_2SiO_2$ with a certain surplus left over.

The amount of CaO in the slag must also suffice to form other mineral compounds, such as $CaO \cdot Fe_2O_3$ (calcium ferrite), $CaO \cdot Al_2O_3$ (calcium aluminate), etc.

Noting that the formation of stable $(CaO)_4P_2O_5$ is only possible with a phased binding of phosphorus, the dephosphorization reaction can be written as the sum of the following reactions:

$$2[P] + 5(FeO) \rightleftharpoons (P_2O_5) + 5[Fe]; \quad \Delta H = -47{,}850 \text{ cal}$$

$$(P_2O_5) + 3(FeO) \rightleftharpoons (3FeO \cdot P_2O_5); \quad \Delta H = -30{,}600 \text{ cal}$$

$$(3FeO)P_2O_5 + 4(CaO) \rightleftharpoons 4(CaO) \rightleftharpoons (4CaO \cdot P_2O_5) + 3(FeO); \quad \Delta H = -130{,}100 \text{ cal}$$

$$2[P] + 5(FeO) + 4(CaO) \rightleftharpoons (4CaO \cdot P_2O_5) + 5[Fe]; \quad \Delta H = -208{,}550 \text{ cal}$$

Since oxidation of P and fluxing of its oxide occur with the evolution of a large amount of heat, then, according to Le Chatelier's principle, it is advisable to reduce fuel supply to the furnace during the period of dephosphorization of the bath, provided that the high-basic slag is homogeneous and free-running.

The conditions of equilibrium distribution of phosphorus between metal and slag may be written by the equation

$$\log K_P = \log \frac{(a_{Ca_4P_2O_9})}{[P]^2(a_{FeO})^5(a_{CaO})^4} = \frac{40{,}067}{T} - 15.06$$

This expression of the constant allows us to draw the following conclusions:

(1) the residual content of phosphorus in the steel depends on the P_2O_5 content of the slag. Therefore, the higher the phosphorus content of the charge, the more difficult it is to reduce its concentrations in the metal;

(2) the higher the FeO and CaO concentrations in the slag, the lower the residual phosphorus content of the metal will be.

Lowering the process temperature also favours dephosphorization of the metal, since the value of K'_P falls with drop in temperature. But these conclusions, based on thermodynamics, however, suffer from a certain conditionality, since a high basicity of the slag is only obtainable through CaO at the high temperatures required to make the slag fluid, and without which its activity as regards dephosphorization is lost.

For given concentrations of MnO and MgO in the slag, its basicity can be increased by additions of CaO only to a definite level, since when the sum (%CaO — %MgO + + %MnO) = 60 per cent, this will cause the formation of heterogeneous slags. For that reason, the concentration of CaO in final slags must not exceed 45-48 per cent even after slagging-off twice.

As has been shown experimentally, the CaO/FeO ratio in dephosphorizing slags cannot be arbitrary; the experimentally found curves reveal certain maxima for the distribution coefficient $\%(P_2O_5)/\%[P]$ as a function of (FeO) in the slag, the amplitudes of these maxima increasing as the basicity of the slag rises (Fig. 87).

The effect of MnO in the slag on the process of dephosphorization is shown in Fig. 88. As will be seen, an increase in MnO results in lowering the maxima on the dephosphorization versus FeO concentration curves; and, besides, the maxima (332, 274, and 228, for MnO concentrations of 1.5, 5.5 and 11.0 per cent, respectively) are proportional to the corresponding CaO concentrations (49, 43, and 41 per cent). Hence it follows that MnO influences dephosphorization simply by diluting the slag.

As regards Al_2O_3, its increasing concentration leads to the reduction in the distribution coefficient $\%(P_2O_5)/\%[P]$ probably due to the formation of calcium aluminate, so that the role of Al_2O_3 is the same as that of SiO_2.

The distribution coefficient $\%(P_2O_5)/\%[P]$ has been found to rise with FeO concentration for a given CaO level in the slag.

Some researchers assume that dephosphorization occurs more readily if free CaO is present in the slag. Calcium orthosilicate is capable of dissociating by the reaction

$$(4CaO \cdot 2SiO_2) \rightleftharpoons 2CaO \cdot 2SiO_2 + 2(CaO)$$

which, in their opinion, would explain why free CaO is always present in the slag. They have proposed to take the value $(4CaO \cdot P_2O_5):[\%P]^2=100$ which enters the expression for the equilibrium constant as an index of dephosphorization.

The oxides MnO and MgO, as well as CaO, promote dephosphorization, while CaF_2 has no effect on the equilibrium constant and forms a complex compound $4CaO \cdot P_2O_5 \cdot \cdot CaF_2$. Its useful effect lies only in improving the solubility of CaO in the slag. The indirect effect of Al_2O_3 on dephosphorization is similar to that of CaF_2.

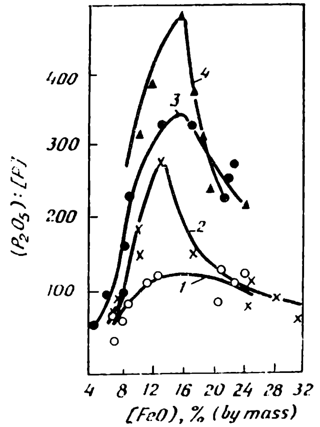


Fig. 87. The distribution coefficient (P_2O_5) : [P] as a function of slag basicity CaO : SiO_2

1—basicity 2.4; *2*—2.8; *3*—3.5; *4*—4.0

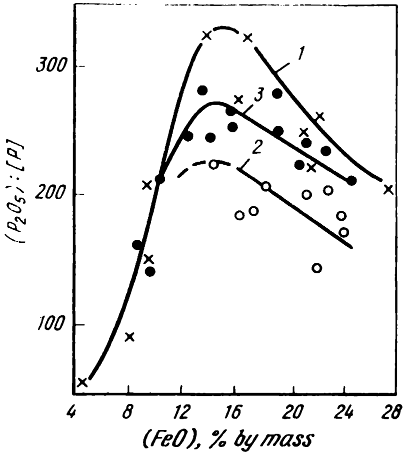


Fig. 88. Effect of (MnO) content on the distribution coefficient (P_2O_5): [P]

1—1.5% MnO; *2*—5.5% MnO; *3*—11% MnO

Figure 89 shows the dependence of the dephosphorization index on slag basicity and FeO content (in molar proportions).

As will be seen from the graph, an increase in the slag basicity through an addition of CaO has an appreciable effect on dephosphorization only at basicity values of 2.75-3.00. Dephosphorization cannot proceed further without increasing the concentration of FeO in the slag.

The effect of the temperature of the process on dephosphorization is illustrated in Fig. 90.

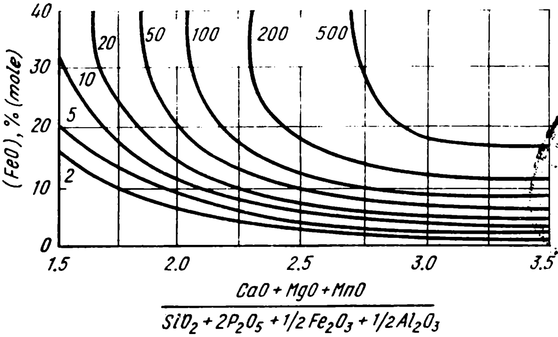


Fig. 89. Dependence of the dephosphorization index on slag basicity and (FeO) content (numbers on curves are index values in mole per cent)

The diagram shows that lowering the temperature by 100°C enables one to achieve the same degree of dephosphorization at a substantially lower basicity. This conclusion is confirmed by puddling practice, where dephosphorization of the order of 75-85 per cent was achieved in the complete absence of CaO, solely through increasing the FeO content of the slag.

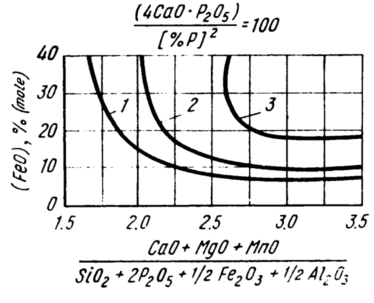


Fig. 90. Dependence of the dephosphorization index on temperature 1—1550°C; 2—1600°C; 3—1650°C

The analytical expression relating the equilibrium constant to temperature

$$\log K = \log \frac{[\Sigma P]^2 (FeO)^5 (CaO)^1}{(\Sigma P_2O_5)} = \frac{51{,}875}{T} + 33.16$$

agrees well with experience of dephosphorization. In this equation (FeO) and (CaO) are taken as 'free' concentrations calculated according to Schenck.

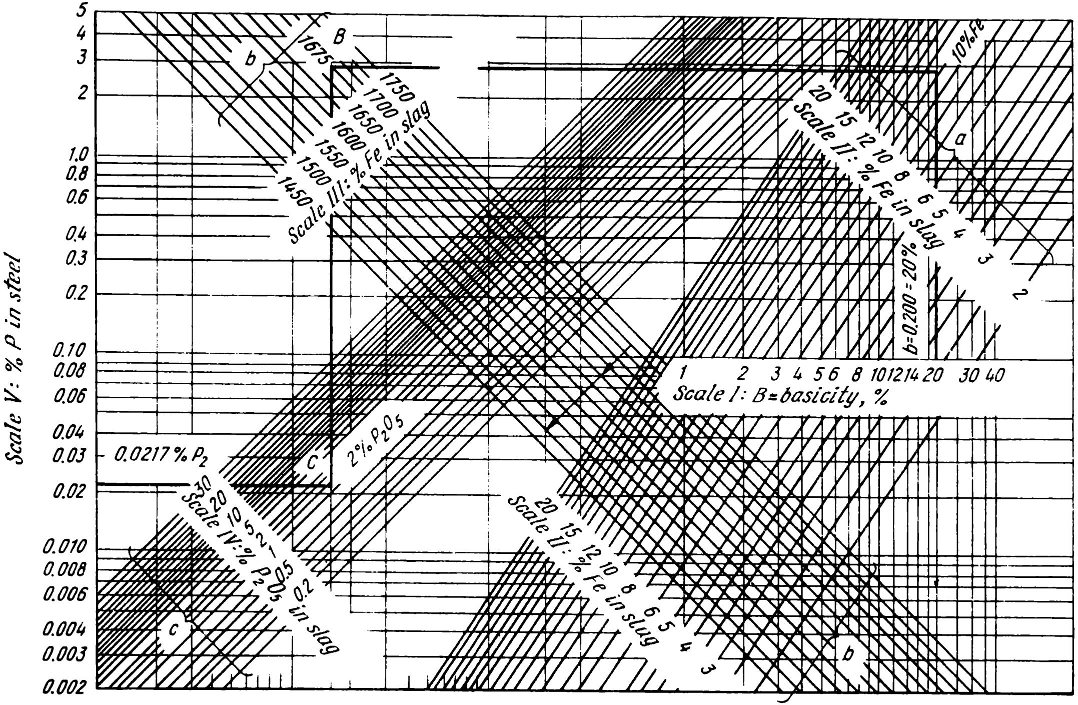


Fig. 91. A nomogram for determining the equilibrium content of phosphorus in steel for a given slag composition and temperature

The expected concentration of phosphorus in the metal at equilibrium with the slag of a given temperature can be conveniently found by using a nomogram (see Fig. 91) constructed from the equilibrium constant

$$\log K = \log \frac{[P]^2 (Fe)^5 B^3}{P_2O_5} = -\frac{24,000}{T} + 3.62$$

where B is the active (free) CaO:

$$B = 0.01\,[(CaO) - 0.93(SiO_2) - 1.18(P_2O_5)]$$

and concentrations are in percentages.

Effect of the bulk of slag. Denoting the phosphorus content of the metal by P_m, that of the slag by (P), and the bulk (or mass) of the slag as a percentage of the mass of metal by b, we have

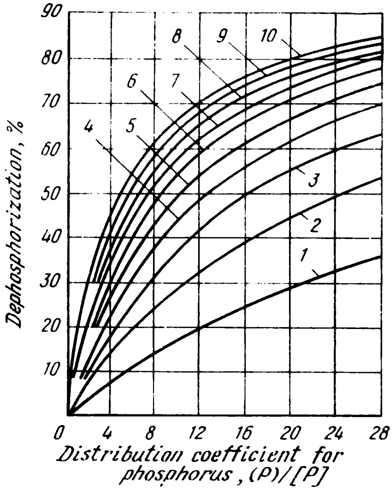


Fig. 92. The effect of the distribution coefficient (P)/[P] on dephosphorization for various amounts of slag. Amount of slag *1*—2%; *2*—4%; *3*—6%; *4*—8%; *5*—10%; *6*—12%; *7*—14%; *8*—16%; *9*—18%; *10*—20%

$$[P] = p_m - (p)\frac{b}{100}$$

This relationship is shown graphically in Fig. 92.

As can be seen, the degree of dephosphorization increases with the bulk of slag for the same coefficient of distribution of phosphorus between slag and metal.

Let the index of distribution of phosphorus between slag and metal be denoted $(\%P_2O_5)/[P] = \eta_P$.

Hence, $[\%P] = (\%P_2O_5)/\eta_P$.

Then, for furnace operation without slagging-off, the balance equation for determining the amount of phosphorus in the charge will be as follows:

$$[\%P]M + \frac{62}{142}(\%P_2O_5)Sl = P_{Sl}$$

or

$$(\%P_2O_5) = \frac{P_{Sl}}{\frac{1}{\eta_P} + \frac{62}{142}Sl}$$

where $[\%P]$ = phosphorus content of steel, %

$(\%P_2O_5)$ = content of phosphorus oxides in slag, %

P_{Sl} = average content of phosphorus in the charge, per cent of the mass of the metallic charge

M = amount of steel, fractions of the mass of the metallic charge (taken as unity)

Sl = amount of slag, per cent of the mass of the metallic charge

For operation with slagging-off, the balance equation is

$$[\%P]M + \frac{62}{142}(\%P_2O_5)Sl = P_{Sl} - P_{off}$$

or

$$(\%P_2O_5) = \frac{P_{Sl} - P_{off}}{\frac{1}{\eta_P} + \frac{62}{142}Sl}$$

where P_{off} = amount of phosphorus removed with skimmed-off slag, per cent of the mass of the metallic charge

The larger the bulk of slag in the furnace and the greater has been the amount of slag skimmed off, the less is the content of P_2O_5 in the remaining slag, and therefore the less the content of phosphorus in the final steel.

It should be remembered, however, that the distribution coefficient for phosphorus depends on the composition of slag.

Dephosphorization with synthetic slags. By the end of the heat the steel and slag are nearing the equilibrium state at which further dephosphorization becomes impossible. This equilibrium can be disturbed outside the furnace by mixing the metal with a slag of a composition that promotes a shift of the equilibrium in the direction of removal of phosphorus from the metal. Slag of the following composition is recommended for treating metal with synthetic slags: 3-10 per cent SiO_2, 60-65 per cent CaO, 20-35 per cent FeO, and some CaF_2. This slag is emulsified better in the metal when the latter is poured onto the slag from a considerable height. In these conditions dephosphorization proceeds very vigorously, and phosphorus content can be reduced from 0.436 per cent to 0.045 per cent, from 0.060 per cent to 0.011 per cent, or from 0.022 per cent to 0.007 per cent.

The degree of dephosphorization depends on the amount of synthetic slag used, which should be 2.5-4.0 per cent of the mass of the steel treated.

The composition of the slag used to treat Bessemer steels is as follows (in percentages): SiO_2 6.4-9.4, Al_2O_3 2.9-9.0, CaO 44.1-53.3, MgO 3.6-12.4, MnO 4.2-7.9, and FeO (scale) 15.0-23.9.

It has been found experimentally that the final basic slags obtained when making rimming steels are suitable for dephosphorization.

In certain conditions, solid powdered mixtures are employed instead of liquid synthetic slags. The composition of the mixture usually consists of scale, lime and fluorspar; the effect obtained is largely dependent on the fineness of the components and the order of adding them: scale → → fluorspar → lime.

Dephosphorization and rephosphorization. Dephosphorization occurs most readily when making rimming steels, because of the high oxidation of the slag, low content of carbon, and low consumption of reducers.

A low phosphorus content in a basic low-carbon killed steel can be obtained without much trouble by properly controlling the slag conditions. When making steels of medium or high carbon content, reduction of phosphorus in the bath requires certain additional operations (slagging off and forming of a new slag), which prolongs the heat and thus increases the cost of steel.

The impurities in the metal (i.e., carbon, silicon, and manganese) and the iron itself can also act as phosphorus reducers in both preliminary and final deoxidation. Examples are known of marked rephosphorization of killed steel during teeming owing to a large bulk of furnace slag in the ladle; for instance, the steel in the fourth runner had 0.084 per cent phosphorus against 0.017 per cent on tapping.

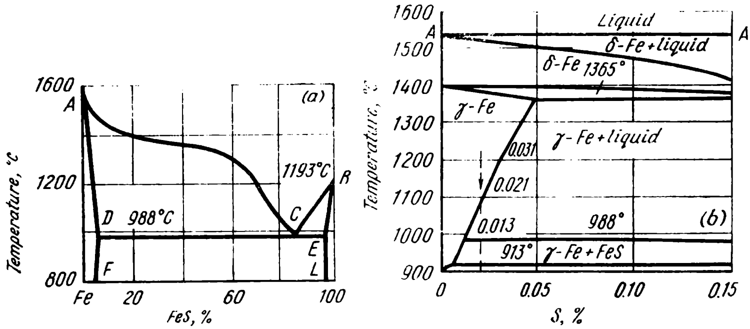


Fig. 93. The Fe-FeS system and the iron corner portion of the Fe-S diagram

Desulphurization. An increased content of sulphur impairs mechanical properties and corrosion resistance of steel and makes it poorly weldable. Sulphur is useful only in automatic steel.

As will be seen from the Fe-FeS diagram (Fig. 93), sulphur has unlimited solubility in liquid iron, but a very low solubility in solid metal. Its solubility in α-iron is negligible, but is appreciable in γ-iron. Thus, its maximum solubility in γ-iron is 0.013 per cent at 1000°C, 0.021 per cent at 1100°C, and 0.031 per cent at 1200°C. As the melt cools the surplus sulphur above the level corresponding to its maximum solubility in γ-iron is concentrated in the liquid phase. At point *C* a liquid and two solid phases can exist in equilibrium in the fusible eutectic (15.4 per cent Fe and

84.6 per cent FeS) at 988°C, their compositions being determined by points *D*, *C*, and *E* on the diagram.

As a result of the selective crystallization in a solidifying melt, iron sulphides, which have a comparatively low melting point (1193°C), or the fusible eutectic Fe-FeS, and also oxysulphides, are concentrated at grain boundaries in the form of films, thus weakening the cleavage of grains; at the temperatures common to rolling or forging (1200-820°C) the sulphides become liquid and cause breakage of steel through red shortness.

It follows from the graph in Fig. 93 that if the steel contains less than 0.01 per cent S, there will be no red shortness, since all the sulphur will be in solid solution with the γ-iron at the temperatures of plastic deformation, and therefore no fusible eutectic will be formed at grain boundaries. At a given sulphur concentration in the steel, the temperature of rolling can be so chosen as to avoid red shortness. With a sulphur content of 0.02 per cent, for example, and a temperature at the end of rolling of 1075°C, there should be no red shortness at all. When the temperature is below that limit, red shortness may occur since the limit of sulphur solubility in the γ-iron will be exceeded and the surplus sulphur will begin to appear at grain boundaries as a fusible eutectic.

Manganese, an element always present in any kind of common steel in an amount of 0.30-0.50 per cent, protects the metal against red shortness during hot forming. Its favourable effect is in that the sulphur separating from the γ-iron solution combines with manganese rather than with iron, thus forming manganese sulphide which remains solid at the temperatures of hot forming (the melting point of MnS is 1620°C).

The effect of the other elements commonly present in iron alloys on the solubility of sulphur has still not been examined thoroughly; they can, however, be divided into three groups as follows:

(1) metals whose sulphides are usually less stable than FeS and therefore have no effect on the solubility of sulphur (copper, nickel, cobalt, and tungsten);

(2) elements—carbon, silicon, and phosphorus—that form compounds with iron and thus reduce the number of moles

of free iron in the melt. The presence of carbon and silicon apparently has a strong negative effect on the solubility of FeS in liquid iron. With a carbon content above one per cent the solubility index is only 5 per cent. With both carbon and silicon present in liquid iron, the solubility of sulphur should reduce even more;

(3) elements whose sulphides are more stable than FeS and which are capable of producing a desulphurizing effect in favourable conditions.

In slags of steelmaking processes, the sulphides FeS, MnS and CaS are most important.

The stability of sulphides can be characterized by the heats of their formation, cal/mol:

$$Fe_l + \frac{1}{2} S_{2_g} = FeS_l; \qquad \Delta H = -28{,}000$$

$$Mn_l + \frac{1}{2} S_{2_g} = MnS_{sol}; \qquad \Delta H = -65{,}000$$

$$Mg_g + \frac{1}{2} S_{2_g} = MgS_{sol}; \qquad \Delta H = -126{,}340$$

$$Ca_g + \frac{1}{2} S_{2_g} = CaS_{sol}; \qquad \Delta H = -166{,}940$$

$$2Cu_l + \frac{1}{2} S_{2_g} = Cu_2S_l; \qquad \Delta H = -27{,}920$$

$$Mo_{sol} + \frac{1}{2} S_{2_g} = MoS_{sol}; \qquad \Delta H = -76{,}300$$

$$W_{sol} + S_{2_g} = WS_{2_{sol}}; \qquad \Delta H = -60{,}960$$

It follows from the comparison that manganese has a greater affinity for sulphur than iron and can therefore be effectively used to desulphurize pig iron. Aluminium, chromium, titanium, and zirconium also have the power to desulphurize iron.

The solubility of sulphides in slag, which is very low in acid slags but rises with an increase of basicity, is of great significance for desulphurization.

It must be noted that FeS is highly soluble in the metallic phase, MnS only slightly soluble, while CaS is practically insoluble.

Effect of manganese on desulphurization. With a quite high concentration of manganese in pig iron, desulphurization in the hearth of a blast furnace and on tapping occurs as FeS → MnS → CaS, and in the iron ladle, as FeS → MnS. As has been found, pouring of iron from large ladles (90 tons) into smaller ones causes a substantial drop of the sulphur content. When pig iron with a high content of both manganese and sulphur solidifies, a lowering of the content of both is observed owing to segregation of MnS. The solubility of this sulphide in liquid iron is limited by the equilibrium conditions of the reaction

$$MnS = Mn_l + S_l$$

whose constant can be expressed as

$$K' = [\%Mn] \cdot [\%S]$$

In steel this reaction proceeds very weakly, which can be explained by the higher temperature and also by the lower contents of carbon and silicon, as compared with pig iron.

As regards pig iron, the reaction

$$FeS + Mn = MnS + Fe; \quad \Delta H = -21{,}700 \text{ cal}$$

occurs in the mixer at a comparatively low temperature and its desulphurizing effect becomes more pronounced with an increase in the manganese content of the pig iron.

Note that MnS separates out as a solid solution in FeS rather than in the pure form

$$(FeS) + [Mn] \rightarrow [Fe] + (Fe, Mn)\,S$$

thus forming complex sulphide and oxysulphide inclusions in the metal. A desulphurizing effect of this reaction becomes noticeable in steelmaking processes only when the Mn content of pig iron is 2 per cent or higher. Desulphurization is favoured by skimming-off the slag from the mixer twice a day.

A certain degree of desulphurization is attained in the mixer also as the result of the formation of gaseous SO_2 through the exothermic reactions of the oxidizing atmosphere and the sulphides of the slag:

$$3\,(FeS) + 5O_2 = (Fe_3O_4) + 3SO_{2_g}$$

and

$$3(MnS)+5O_2 \quad (Mn_3O_4)+3SO_{2_g}$$

The mechanism of the desulphurization of steel in the open-hearth bath is assumed to be as follows:

(1) diffusion of iron sulphide from steel to slag

$$[FeS] \rightarrow (FeS)$$

(2) reactions in the slag

$$(FeS)+(CaO) \rightleftarrows (CaS)+(FeO)$$

$$(FeS)+(MnO) \rightleftarrows (MnS)+(FeO)$$

The homogeneous reactions in the slag proceed at a higher rate, unlike the diffusion process. Thus the sulphur is brought to equilibrium between the steel and slag much more slowly than the other elements in the bath.

The weak desulphurizing action of Mn at its normal concentrations in steel is clearly illustrated by calculations. The percentage concentrations of FeS in steel at 1600, 1500, and 900°C, as a function of manganese content, are given in Table 38, from which it will be seen that the transition from FeS to MnS is intensified with lowering of the temperature and increase of the manganese concentration.

Table 38

FeS in Steel as a Function of Mn Content and Temperature

Mn content, (percentages)	FeS content (percentages), at various temperatures, °C		
	1600	1500	900
0.10	97.4	96.2	34.1
0.25	93.8	91.2	17.2
0.50	88.1	83.7	9.3
1.00	78.8	72.0	4.9
2.00	64.9	56.3	2.5

Since FeS has a higher solubility than MnS, the addition of manganese ore to slag is an effective means of desulphurization, the reaction $FeS + MnO \rightarrow MnS + FeO$ being then shifted to the right.

Technique of desulphurization. The equilibrium between steel and slag

$$[FeS] \rightleftarrows (FeS)$$

is established through diffusion, which is rather slow, its rate largely depending on the physical state of the slag, i.e., its fluidity. But the decisive factors affecting desulphurization are the slag basicity and the surplus of free CaO for development of the homogeneous reaction

$$(FeS) + (CaO) \rightarrow (CaS) + (FeO)$$

i.e., the maximum concentration of CaO and the minimum concentration of FeO in the slag are required for the complete transformation of FeS, which is soluble in metal, into practically insoluble CaS. This explains high degrees of desulphurization attainable in blast furnaces and electric furnaces. With a reducing atmosphere, the following reactions occur:

in blast furnaces and electric furnaces

$$FeS + CaO + C \rightarrow Fe + CO + CaS$$

in electric furnaces only

$$FeS + CaC_2 + 2FeO \rightarrow CaS + 3Fe + 2CO$$

or

$$FeS + CaO + C \rightarrow Fe + CaS + CO$$

In the basic open-hearth process, the basicity of slag, as the most important factor of desulphurization, is largely counteracted by the FeO present in the slag. The distribution coefficient for sulphur then cannot be high and is usually within the limit of 6 to 8 (at most 10).

The coefficient η_S can be calculated approximately from the chemical composition of slag by the following formula:

$$\frac{(S)}{[S]} = N_S\left[2.6 + 1.6\frac{(CaO')}{(FeO)}(\vartheta' - 2) + 11.0[Mn]\right]$$

where (S), [S], and [Mn] contents of these elements, percentage by mass

ϑ' = the basicity: $\vartheta' = \frac{CaO - 4P_2O_5}{SiO_2} \quad \frac{CaO'}{SiO_2}$

N_S = total number of moles per 100 g of slag, calculated by the formula

$$N_S = (SiO_2) + (MnO) + (FeO) + (P_2O_5) + 0.21\,(\vartheta' - 2)\,(CaO')$$

Effect of the bulk of slag and sulphur in lime. Denoting the content of sulphur in pig iron and scrap by $\%S_{ch}$ and its content in lime $\%S_l$ (as percentages of the mass of the charge) and the amounts of metal and slag as M_m and M_{sl}, respectively, we can write the following balance equation:

$$\%S_{ch} + \%S_l = M_m[\%S] + M_{sl}(\%S)$$

The coefficient of distribution of sulphur between slag and metal is

$$\eta_S = \frac{(\%S)}{[\%S]} \quad \text{or} \quad (\%S) = \eta_S[\%S]$$

Substituting the content of sulphur in the slag into the former equation we get

$$[\%S] = \frac{\%S_{ch} + \%S_l}{M_m + M_{sl}\eta_S}$$

Hence it follows that the final steel will be low in sulphur if the sulphur contents of pig iron, scrap and lime are low, and also if the yield of liquid metal and the bulk of slag are high.

The greater the bulk of slag of a definite basicity in the bath, the more sulphur will pass into it from the metal at a given stable distribution coefficient η_S, since the amount of residual sulphur in steel is proportional to the sulphur concentration in the charge (S_{ch}) and inversely proportional to the distribution coefficient η_S and the bulk of the slag.

In common charging practice, however, the permissible amount of slag does not exceed 10 to 12 per cent of the mass of the metal, so that at best with $\eta_S = 10$ and with 10 per cent of the bulk of slag, it is not possible to remove more than 50 per cent of the sulphur without slagging-off.

Thus, it can be concluded that the following conditions must be ensured to keep the sulphur content to a minimum:

(1) a minimum amount of sulphur in the charge materials;

(2) slag and thermal conditions at which the distribution coefficient η_S is maximal;

(3) running the furnace with a maximum of slag or, which is more effective, skimming-off the slag and adjusting a new one;

(4) intense boiling of the bath and no noticeable inflow of sulphur with the fuel.

In the light of the foregoing, the problem of refining steel from sulphur must be mainly solved at a preliminary stage by curing pig iron in an inactive mixer or at stations of treatment of pig iron where it is desulphurized with soda, or by blowing in a mixture of lime and aluminium powder (or coke dust), magnesium and calcium carbide.

Desulphurization outside the furnace. The use of synthetic slags to treat liquid metal in a ladle is considered in more detail in Chapter 18, where it is noted that with a suitable chemical composition (in particular with a low content of FeO + MnO) the basic slags used for deoxidation also have a desulphurizing effect.

Experience has proved that carbide slags, white slags, and especially lime-alumina slags are very effective in this respect.

In experiments with the use of preliminarily melted carbide slags of the following percentage composition: SiO_2 13, MgO 4, Al_2O_3 2, CaF_2 15, CaO 62, CaC_2 1, FeO under 1.0, and MnO under 0.2, the sulphur content of basic steel was lowered by 60-67 per cent. When the same slags were added as powders, sulphur content was reduced by 40 per cent (Table 39).

According to some researchers, slag must have a percentage composition close to the following, in order to remove both oxides and sulphides from the metal: SiO_2 15-20, Al_2O_3 30-40, CaO 40-44, MgO 0-8.0, FeO 0.5-0.8, and MnO 0.5-1.2.

The Central Research Institute for Ferrous Metallurgy (TsNIIChM) has carried out many joint experiments with steel works on treating open-hearth, Bessemer and electric

Table 39

Variation of Sulphur Content after Treating Metal with Carbide Slags

Carbide slag	S in metal (per cent)	
	before treatment	after treatment
Melted in separate furnace	0.036	0.014
	0.056	0.022
Powdered slag	0.049	0.030

furnace steels in ladles with molten lime-alumina slags in order to remove sulphur and non-metallic inclusions.

The metal to be treated and deoxidized in the ladle has an increased oxygen content upon tapping (0.006-0.007 per cent for the grade ШХ15 and 0.02-0.03 per cent for low-carbon steel).

The slag having a composition of 52-53 per cent CaO, 44-45 per cent Al_2O_3, 1.0-1.2 per cent SiO_2, 0.15-0.18 per cent FeO, and 0.85-0.90 per cent MgO is used in an amount of about 5 per cent of the mass of the melt. It has been found that irrespective of the grade of steel being produced and its initial sulphur content (0.04-0.015 per cent), the treatment with slags results in the sulphur content brought down to 0.005-0.007 per cent for high-carbon steels and to 0.007-0.012 per cent for low-carbon ones. Lower contents of oxygen and non-metallic impurities were also obtained.

A good refining effect is promoted by the extended contact surface between steel and slag, since steel is poured from a considerable height into the ladle previously primed with synthetic slag.

Identical results have been obtained by vacuum slag treatment of transformer steel with final electric-furnace slags.

In treating open-hearth metal with slag outside the furnace, the degree of desulphurization is largely affected by slag fluidity which determines the degree of emulsifying of the slag when mixed with the metal.

Various methods of removing sulphur from pig iron outside the furnace before supplying pig iron to steelmaking furnaces have also found application.

One of the most widely adopted methods is to treat pig iron and various grades of steel with lime, fluorspar and soda (Na_2CO_3), which causes sulphur to pass from the metal to the slag by one of the following reactions:

$$Na_2CO_3 + [FeS] + [C] = (Na_2S) + [Fe] + CO_2 + CO$$

or

$$Na_2CO_3 + [FeS] + 2[C] = (Na_2S) + [Fe] + 3CO$$

Various methods of treating pig iron with powdered lime are widely employed in the USSR, FRG, and Sweden.

Work has been carried out on improving the method of removal of sulphur from liquid iron by injecting powdered lime (or calcium carbide) by a nitrogen jet. The treatment by this method in the ladle gives a high degree of desulphurization in a short time (approx. 3 minutes). In Czechoslovakia in use is the treatment of pig iron with a slag-forming mixture (80 per cent CaO and 20 per cent CaF_2), which reduces the sulphur content by 82 per cent. The presence of silicon and carbon in pig iron favours desulphurization which proceeds even more intensely if small amounts of powdered aluminium or magnesium (2 per cent of the mass of lime) are added together with CaO. Magnesium is not only an effective deoxidizer, but also a desulphurizer. At some Soviet works, magnesium in pigs is added into liquid iron in the ladle under a cap; at others, granulated magnesium is blown with lime into liquid iron.

A relation between desulphurization and deoxidation has been proved experimentally. It has been found that the product of carbon and sulphur contents in the metal (iron or steel)

$$[\%C] \cdot [\%S] = 0.011$$

is constant and almost independent of temperature within the temperature range of 1420°-1720°C.

Taking into account the known equilibrium relation

$$[\%C] \cdot [\%O] = 0.0025$$

in the range of temperatures from 1580 to 1620°C, we get

$$[\%S]:[\%O] \approx 4 \quad \text{or} \quad [\%S] \approx 4\,[\%O]$$

which relates the sulphur content in carbon steel to the concentration of dissolved oxygen.

Sources of sulphur. The sources of sulphur in open-hearth steels are the metallic and non-metallic materials of the charge and the fuels, both liquid and gaseous.

Experiments with fuels labelled with the isotope S^{35} have shown that sulphur is absorbed by the bath and only part of it is carried directly away with furnace gases, the bath picking up 18-32 per cent and the slag, 38-57 per cent of the sulphur.

An increase in the excess air for fuel combustion reduces the sulphur content of furnace gases and thus diminishes its harmful effect, but as more air is supplied, the thermal effect of the fuel declines and furnace productivity lowers. A way out is to burn the fuel in oxygen-enriched air because part of the sulphur will then be removed in gaseous form.

Oxidation of carbon. We have already considered the conditions for the passage of oxygen into the slag from the furnace atmosphere and for its movement in the slag to the slag-metal interface. The further process of carbon oxidation in the bath consists of three stages:

$$(FeO) \rightarrow [FeO] \qquad (1)$$

$$[FeO] + [C] \rightarrow [Fe] + [CO] \qquad (2)$$

$$[CO] \rightarrow \{CO\} \qquad (3)$$

$$(FeO) + [C] \rightarrow [Fe] + \{CO\} \qquad (4)$$

Reaction (1), i.e., the transition of oxygen from slag to metal, follows the distribution law. The experimentally found relationship between temperature and the distribution coefficient for slags composed of FeO-MnO is expressed by the equation

$$L_{FeO} = 0.588 \cdot 10^{-4} t°C - 0.0793$$

Reaction (2), i.e., an interaction of FeO and C present in the metal solution, occurs very quickly.

Reaction (3) is the evolution of CO in a gaseous state from the metal.

The modern view is that oxidation of C occurs at the rough solid surface of the hearth or at the boundaries between metal and gases or gas bubbles. Bubbles of carbon monoxide may also be formed in the pores of solid non-metallic inclusions in the bath that have not been wetted by the metal and in the pores of solid components of heterogeneous slag near the metal-slag interface. The size of pores in the hearth and in particles of inclusions must exceed that of the bubbles being formed. All the three processes occur simultaneously, the slowest determining the rate of carbon oxidation reaction as a whole.

At present it may be taken as experimentally proved that reaction (2) can proceed at very high rates. This cannot be said of reactions (1) and (3).

A rise of bath temperature favours acceleration of all the three processes.

According to modern views, molecules of CO, FeO, and Fe_3C cannot exist in a liquid metal solution. Carbon is present in the solution in the form of positively charged particles C^{4+}, while oxygen as anions O^{2-}. The reaction between the carbon and oxygen dissolved in metal occurs at the metal-gaseous phase interface by the formula $[C] + [O] = \{CO\}$, the molecules of CO immediately passing into the gaseous state.

Molecules of $\{CO\}$ can only exist in the gaseous phase. The whole process of carbon oxidation comprises the movement of the oxygen that has passed from the slag to the reaction zone, the chemical interaction between particles of carbon and oxygen, and the removal of bubbles of $\{CO\}$ from the reaction zone.

Since the reaction $[C] + [O] \rightarrow \{CO\}$ can proceed only at the boundary with the gaseous phase, an indispensable condition for the process of carbon oxidation is the presence or formation of a gaseous phase in the bath of an open-hearth furnace. This phase may be formed by gas bubbles, gas in the pores of non-wettable hearth or pores in the materials used in the melt.

Let us find by referring to Fig. 94 where in the bath this reaction can possibly occur with the formation and growth of a bubble: in the bulk of metal, at the surface of contact between the liquid metal and slag, at the surface of contact between the liquid metal and lining, at the surface of gas bubbles or at the surface of contact of the liquid metal with particles of non-metallic inclusions.

Owing to that reaction, the equilibrium pressure of carbon monoxide p_{CO} in the bubble formed must be greater

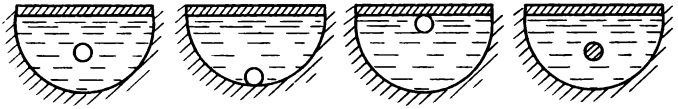


Fig. 94. Diagram showing where gas bubbles are formed in an open-hearth bath

than the total external pressure acting on the bubble, i.e., the sum of the atmospheric, hydrostatic and capillary pressures:

$$p_{CO} \geqslant p_{at} + \gamma_{Fe}h + \gamma_{sl}h + \frac{2\sigma}{r}$$

where p_{at} = pressure in the reaction chamber, equal approximately to 1.001 at

$\gamma_{Fe}h$ and $\gamma_{sl}h$ = hydrostatic pressures of the metal and slag, kgf/cm²

σ = surface tension of the metal, erg/cm²

r = radius of the bubble, cm

The surface tension σ in liquid metal may vary between 1200 and 1600 erg/cm² depending on the carbon content and can be found by the formula

$$\sigma = 1600 - 100 \cdot [\%C], \text{ erg/cm}^2$$

The internal pressure in the bubble increases with a decrease of its radius, but with a very small size of bubbles the capillary pressure can be very great so that the formation of bubbles will be unfeasible. For instance, according to the theory of hole state of a melt, we may assume that if a nucleus of a radius of $r = 10^{-9}$ cm is formed, the capillary pressure at $\sigma = 1000$ dyn/cm should be $2\sigma/r = 2.1 \times 10^{-5}/10^{-9} = 20{,}000$ at. On the other hand, simultaneous presence and effective collision of a tremendous number of carbon and oxygen atoms in a small volume of metal is required for a gas bubble to appear in that volume. This is very unprobable to occur even with a three to five-fold supersaturation of the metal-gas system. All this may indicate that the formation of a CO bubble in a pure metallic bath is largely improbable.

The critical size of a bubble, r_{cr}, is determined by the equality of the total external pressure and the pressure of evolution of carbon monoxide. Under such conditions a bubble begins to form, becomes stable and continues to grow.

According to Frenkel's hypothesis, 'holes' continually appear and instantly disappear in molten metal, and are discontinuities in the liquid. In other words, the liquid metal in the bath is transpierced, as it were, by numerous gas cavities whose number is equivalent to the increase of the volume (approximately 3 per cent) on transition of the solid metal to the liquid state.

Can these gas cavities serve as places of nucleation, formation and dislocation of carbon monoxide bubbles? As is known, the work of formation of a 'hole' is $w = {}^4/_3\, \pi r^2 \sigma$. It has been found from this formula that the radius r of a 'hole' is 10^{-8} cm, i.e., the size of the cavity is quite suitable for dislocation of a molecule of gaseous CO, since the radius is of the same order as the size of the molecule.

But actually this is not so, since the life of a 'hole' is negligible and the CO molecule that has passed into the gaseous state through the reaction $[C] + [O] = CO$ and occupied the cavity immediately dissolves again in the liquid by the reaction $CO \rightarrow [O] + [C]$ under the action of the tremendous external pressure of the liquid, so that the hole is actually disappears. Thus, further coalescence of bubbles and their removal from the metal is impossible, contrary to the hypothesis. Therefore, the formation of bubbles by the reaction $[C] + [O]$ in the metal is unfeasible.

For the same reason it is unlikely that this reaction and the formation of CO bubbles will occur at the interface between the liquid pure metal and fully molten homogeneous slag, i.e., at the interface between two mutually wettable homogeneous phases.

The reaction [C] + [O] and formation of bubbles are possible on the rough surface of the hearth and banks (as has been found experimentally, the wetting angle of liquid metal on a smooth surface of magnesite is 151-157 degrees). This was proved experimentally in the heats carried out at a high temperature with the melt intentionally supersaturated with oxygen relative to its carbon content. The reaction of decarbonization did not started until the glazed surface on the walls of a quartz crucible was removed by means of a glass rod, i.e., until contact was ensured between the metal and the roughed unwettable surface of the crucible.

This, without doubt, is the active front of the reaction of carbon oxidation and formation of CO bubbles. It is probable that after the latent period of accumulation of the reaction products, the nucleation and growth of bubbles to a size above the critical one occur quite quickly and intensively, which facilitates their passage through the dangerous period of deceleration of growth at the initial stage, since at a negligible radius of a bubble the capillary pressure $2\sigma/r$ is rather high. This front of the reaction remains active even in cases of a low volume of gas evolution. As is known, bubbles of a lens-like shape with a large radius of curvature are likely to be formed under these conditions, and therefore the influence of the capillary pressure is not so high in that case.

The reaction [C] + [O] can also occur on the surface of contact between the liquid metal and solid non-metallic inclusions suspended in it or solid particles of ore and lime if these have not been dissolved completely in the slag. The possibility of this reaction and of nucleation of CO bubbles at these interfaces can be explained by the fact that any solid surface has pores, rough places and capillaries. Bubbles can nucleate on those sections of a surface where gas-filled pores are present. But these pores must be suitable for dislocation of bubbles, i.e., their size must be slightly larger than the critical size of bubbles.

As can be seen from Fig. 95, the 'suitable size of pores' varies during a heat, depending on the current concentrations of carbon (oxygen), temperature (which affects surface tension of the metal), and hydrostatic pressure over the pores. For instance, given a bath 1000 mm deep, a metal temperature of 1600°C, a calculated wetting angle between metal and hearth lining of 90 degrees, the content of oxygen dissolved in liquid metal of 0.025-0.002 per cent (at carbon concentrations from 0.1 to 1.0 per cent), and surface tension of 1000-1200 erg/cm^2, the critical size of pores can vary by a curve such as shown in Fig. 95. As will be seen, with the carbon content of 0.2-1.0 per cent in the metal, the radius of active pores which can serve as nucleation centres for gas bubbles is roughly 0.01 cm. It also follows from the figure that large-size pores are required for nucleation of bubbles when a soft metal (such as Armco iron) is being made, since nucleation is limited here by the rate of supply of carbon particles to the reaction zone.

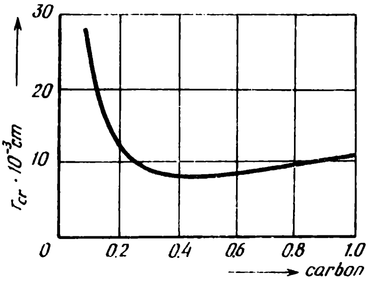


Fig. 95. Dependence of critical size of pores on carbon content of the metal

It then becomes clear why it is difficult to oxidize the last portions of carbon when making soft steels (below 0.04 per cent C), so that special techniques are resorted to, for instance, blowing of the bath with oxygen, addition of sheet or strip metal cuttings, or scratching of the hearth with a steel rod in order to increase the surface roughness and raise the number of nucleation centres.

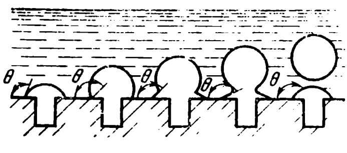


Fig. 96. Variations of the shape of a bubble during its growth

As is shown in Fig. 96, a new gas bubble grows in volume and the wetting angle increases until the Archimedean lifting force becomes greater than the forces of adhesion that retain the bubble at the point of its nucleation. Then the bubble detaches along the neck perimeter in the weakest place and floats up in the liquid metal, and on moving upwards, acquires the shape of an ellipse, lens or mushroom, and can follow very diverse paths due to collisions with other bubbles. At the moment of detachment the radius of a bubble may be 0.55 cm at $\sigma = 1600$ erg/cm^2 and $\gamma = 7.8$ g/cm^3. After detachment of the bubble, the nucleus remains in the pore on the unwettable solid surface and forms a new bubble. During lifting, bubbles can coalesce with each other.

The growth of bubbles of carbon monoxide in points of nucleation and during their lifting occurs owing to the diffusion of atoms of hydrogen and nitrogen dissolved in the metal into their volumes. At the surface of bubbles these atoms combine into molecules. Bubbles also grow owing to active collisions of particles of oxygen and carbon at their surface, these collisions resulting in the formation of carbon monoxide which passes into the bubble. In addition, the hydrostatic pressure in a bubble decreases and its volume increases as the bubble is floating up in the bath. When the bubble reaches the size of 5-6 mm, the nature of its motion begins to vary sharply. The bubble changes its spherical shape to an ellipsoidal one, the minor axis of the ellipsoid being directed along the path of motion. At the same time the bubble begins to vibrate and follows a spiral path in its further movement upward. The speed of motion of bubbles of an average size of 6-15 mm is independent of their diameter and equals 28-30 cm/s, never increasing to more than 35-40 cm/s. Large bubbles, of a size of 30-40 mm, are unstable and disintegrate into smaller bubbles in the upper layers of the bath.

Thus, a very large number of gas bubbles (of an order of $600\text{-}700 \cdot 10^3$) can form every second in the open pores of the rough surface of a clean unslagged hearth of a basic open-hearth furnace with the metal heated up above 1470°C.

It is assumed that on detachment of bubbles from vertical walls no nuclei remain in pores.

According to the calculations made for various depths of the bath at a temperature of 1600°C and various degrees of bath oxidation, the critical radius of bubbles varies from 0.6 to $2.0 \cdot 10^{-3}$ cm. Bubbles are initially of a spherical shape, but then change their shape as the difference between the ferrostatic pressures at their upper and lower portions becomes noticeable.

The reaction of carbon oxidation can also occur on solid nonmetallic inclusions. If a large particle of a solid nonmetallic inclusion has pores of a suitable size, these without doubt can serve as nucleation centres.

This situation is likewise true for the contact surface between liquid metal and solid particles in a heterogeneous slag (solid particles of lime and ore). If these particles have pores of a suitable size, they can become nucleation centres for gas bubbles, thus causing what is called sub-slag or weak boiling.

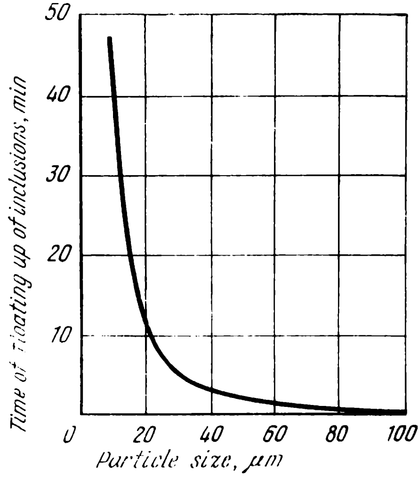


Fig. 97. Duration of floating up of nonmetallic inclusions in a liquid bath 1000 mm deep

Consequently, only large nonmetallic inclusions present in the bath after meltdown can serve as nucleation centres, provided that there are pores of suitable size in them. On the other hand, it is known that large inclusions float up relatively quickly from the metal to slag. There are some calculated data on the duration of floating up of inclusions of various size. As follows from the curve in Fig. 97, lifting of large inclusions from the metal to slag after meltdown takes up not more than 5 minutes. Therefore, the solid nonmetallic inclusions left in the melt soon after meltdown are so small that can hardly have pores suitable for bubble nucleation and thus cannot play any substantial part in the formation of gas bubbles.

Analysis of nucleation of bubbles has shown that the main front for the reaction of carbon oxidation after meltdown is the large surface of the hearth and banks in the bath and possibly large solid nonmetallic inclusions still floating up to the slag.

If a homogeneous slag has been well formed by the moment of meltdown, gas bubbles generated through bottom boiling increase in their volume during floating up and penetrate the slag quite intensively without foaming it, since they are not retained by the slag.

If, however, the slag has had no time to form well and become fluid and homogeneous by the moment of meltdown, it may still contain solid particles of lime and ore. Then under certain conditions gas bubbles will start to form on the contact surface between these particles and the metal. These bubbles instantly pass into the slag when they are not yet sufficiently formed since they have no time to absorb other gases (hydrogen and nitrogen) from the metal, so that the reaction of carbon oxidation will not develop to its full extent on their surface too. These weakly developed bubbles cannot pierce the slag and are retained by the latter or slowly float up in it, thus causing foaming. Surface boiling of the metal always causes foaming of the slag, since the total volume of the bubbles passing into the slag per unit time is much larger than the volume of the bubbles which manage to pass through the viscous slag.

The cold run of a heat or poor slag conditions always cause foaming. After heating up the bath well with a careful increase of the thermal load and with addition of a small amount of ground 45-per cent ferrosilicon, the slag soon becomes fully fluid, the foam gradually disappears, and the front of boiling dislocates from the lower surface of the slag to the banks and hearth. The quicker one manages to suppress foaming, the easier the harmful effect of surface boiling can be eliminated. The factors that make the slag foam stable are still not studied thoroughly. One of the possible factors may be surface-active substances which form firm films on slag-gas interfaces. It is assumed that the components causing foaming of the slag are FeO, Fe_2O_3, V_2O_5, and Cr_2O_3.

In the open-hearth furnace, the reaction

$$[FeO] + [C] \rightarrow Fe_l + \{CO\}$$

occurs only to the right, the inverse reaction being impossible.

The analysis made above relates only to one of the three possible ways of oxidation of carbon, i.e., to the homogeneous reaction of oxidation of reagents in the metallic solution.

The rate of consumption of oxygen for carbon oxidation exceeds the rate of passage of FeO from slag to metal and the rate of its penetration into the deeper layers of the metal. This is confirmed by the long duration of carbon oxidation when making low-carbon steel in large-capacity furnaces with deep baths. The reaction of carbon oxidation is limited by the process of evolution of CO from the metal solution into an independent gaseous phase.

The fact that bottom boiling is predominant in an open-hearth furnace is confirmed by a number of factors, e.g. a relatively uniform composition of the metal over the depth of the bath, which can be explained only by mixing of the metal passing from the deeper layers; vigorous ejection of gas bubbles from the metal through the slag, and a frequently observed phenomenon of intense boiling over an eroded portion of the hearth, i.e., demonstration of the effect of active pores in the bottom.

Thus, certain conditions are required for the process of carbon oxidation to proceed at an appreciable rate, namely a sufficiently high temperature for the occurrence of the homogeneous reaction, passage of oxygen from the slag to metal, and a rough surface of the bottom and banks.

The oxidation of carbon in an open-hearth bath is the principal reaction whose role is exclusively great. The reaction causes bubbling of the bath owing to the passage of small gas bubbles through the liquid and thus facilitates heating of the bath to the required temperature. Boiling is also responsible for degassing of the bath and removal of nonmetallic inclusions by gas bubbles, and also for coagulation and coalescence of nonmetallic inclusions.

Let us now consider the thermal effect of the reaction. Written in a generalized form, the heterogeneous reaction

$$(\mathrm{FeO}) + [\mathrm{C}] \rightarrow [\mathrm{Fe}] + \{\mathrm{CO}\}$$

is endothermic and occurs with a high thermal effect (approximately 38,000 cal).

The experimental studies of the homogeneous reaction

$$[\mathrm{FeO}] + [\mathrm{C}] = [\mathrm{Fe}] + \{\mathrm{CO}\}$$

for the reagents present in the solution have shown that this reaction should be considered weakly exothermic.

With the homogeneous reaction in the metallic phase, the heat of dissolution of graphite (consuming 13,460 cal/mol) and the heat of dissolution of ferrous oxide (consuming 29,460 cal/mol) must be taken into account:

$$\begin{array}{ll}
\mathrm{FeO}_l + \mathrm{C}_{gr} \rightarrow \mathrm{Fe}_l + \mathrm{CO}_g; & \Delta H = 38{,}000 \text{ cal/g-atom} \\
[\mathrm{C}] \rightarrow \mathrm{C}_{gr}; & \Delta H = -13{,}460 \text{ cal/g-atom} \\
[\mathrm{FeO}] \rightarrow \mathrm{FeO}_g; & \Delta H \quad -29{,}460 \text{ cal/g-mol} \\
\hline
[\mathrm{FeO}] + [\mathrm{C}] \rightarrow \mathrm{Fe}_l + \{\mathrm{CO}\}; & \Delta H = -4\,920 \text{ cal/g-atom}
\end{array}$$

According to this calculation, the resultant homogeneous reaction has only a small positive thermal effect, which indicates that the proper course of the reaction depends on kinetic rather than thermodynamic factors.

In view of the complexity of the physico-chemical interaction occurring in the three-phase system and therefore the low accuracy of experimental results, the problem cannot be considered completely solved. Research into the equilibrium of the Fe-O-C system continues.

The results of studies of equilibrium of the C-O system at various pressures made by a number of investigators in laboratory conditions are given in Fig. 98.

Boiling of the bath is an indication that the system is not in equilibrium, which is characterized by the constant product

$$[\%\mathrm{C}] \cdot [\%\mathrm{O}] = m = 0.0025$$

at 1540-1620°C and at low concentrations of carbon, or by

$$[\%\mathrm{C}] \cdot [\%\mathrm{FeO}] = m = 0.0112 \text{ at } 1600°\mathrm{C}$$

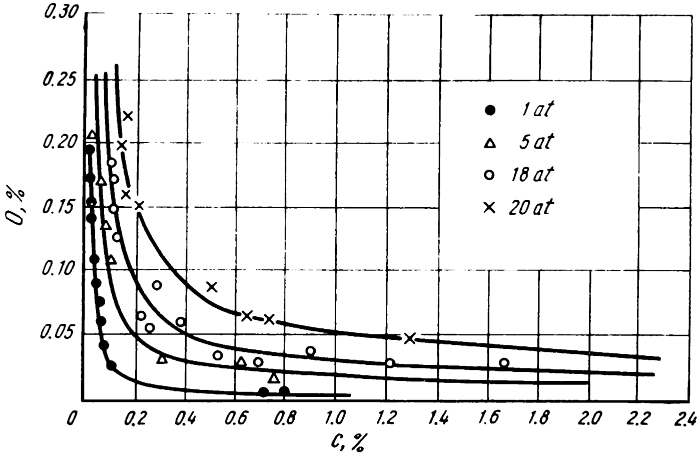


Fig. 98. Equilibrium of carbon and oxygen levels at 1540°C and various pressures

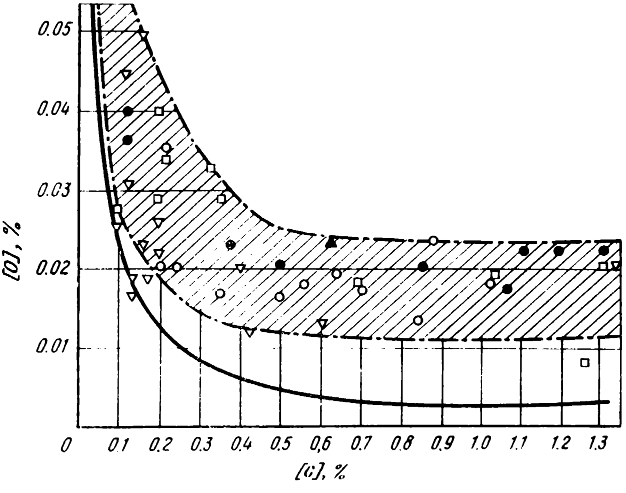


Fig. 99. Relationship of carbon and oxygen in equilibrium and at actual conditions in a molten bath, according to various authors
● -Oiks, Maksimov, and Kaluzhsky; ○—Stark and Chelishchev; △—Oiks; □—Ageev

In a study carried out under the conditions of an open-hearth melt, it has been found that the equilibrium curves differ substantially from the actual total concentrations of oxygen in the boiling bath (Fig. 99). As will be seen from the graph the oxygen concentration remains above the equilibrium value as long as the oxidation reaction continues.

This may be explained by the continuous inflow of oxygen from the furnace atmosphere through the slag into the bath owing to the tremendous pressure gradient of oxygen in these phases, as has been indicated earlier. But, in spite of the continuous inflow of oxygen from slag to metal, the bath is closer to equilibrium as its concentration of carbon lowers. Having a high affinity for oxygen at open-hearth furnace temperatures, carbon takes up the oxygen supplied to the bath and removes it in the gaseous state mainly as carbon monoxide, carbon dioxide accounting for a very small fraction.

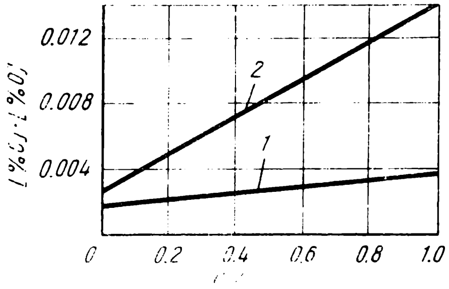


Fig. 100. [%C]·[%O] product as a function of carbon concentration at a pressure of 1 at

1—at equilibrium; 2—average for the bath

Experimental graphs (Fig. 100) of [%C]·[%O] products as a function of carbon concentrations at equilibrium of the system and at average concentrations actually observed clearly illustrate the following: the product [%C]·[%O] is not a constant, but increases with an increase of carbon concentration. From this it follows that the reaction between carbon and oxygen in the open-hearth furnace does not reach equilibrium and that there is usually an excess of dissolved oxygen in the bath.

The author has established the relationship between the absolute concentrations of carbon and oxygen in the bath for the scrap-and-ore process during finishing, which may be expressed by the equation

$$[\%O]\cdot[\%C] = 0.0035 + 0.006\,[\%C]$$

Chapter Fourteen

MODIFICATIONS OF THE BASIC OPEN-HEARTH PROCESS

VARIETIES OF THE PROCESS

Open-hearth furnaces may be used for converting pig iron and scrap of various composition and in any proportions, the composition of the charge determining three main varieties of the open-hearth process as follows.

1. The pig-and-scrap process, in which the charge consists mainly of steel scrap or return scrap from rolling mills. The process is usually employed in open-hearth shops of steel-making and machine-building works located in large industrial centres where steel scrap is available in large quantities, but there is no own production of liquid pig iron. The charge for the process is composed of 68-75 per cent steel scrap, 25-32 per cent purchased iron (in pigs), a small amount (1-2 per cent) of iron ore, and 3-4 per cent limestone to speed up dephosphorization and formation of the final slag. The pig-and-scrap process may also be carried out with the use of liquid metal premelted in hot-air or oxygen-blown cupola furnaces or other plants.
2. The scrap-and-ore process, in which the charge consists of 55-75 per cent liquid iron, 25-45 per cent steel scrap, 12-14 per cent iron ore, and 8-12 per cent limestone. The process is used for making steel at large iron and steel works having their own blast furnaces.
3. The pig-and-ore process, with the charge consisting of 100 per cent liquid pig iron with small additions of iron ore and limestone. The process is almost abandoned in modern practice, with the pig-and-scrap process being used instead.

Scrap requirements. Reverted scrap (waste metal and rejects) of all the metallurgical and mechanical shops of one and the same works can be accurately sorted out according to its chemical composition. Purchased scrap, however, is mostly indeterminate as regards its composition. Turnings from mechanical shops and sheet-metal scrap, especially rusty roofing iron, can introduce a great deal of iron oxides into the charge, and may also be contaminated with soil and sand, which affect slag composition and increase the bulk of slag.

Turnings stacked for a long time in the open air acquire properties similar to those of iron ore and usually become rich in sulphur through the action of SO_2 from the atmosphere:

$$4Fe + 3SO_2 + nH_2O + 4^1/_2O_2 = Fe_2(SO_4)_3 + Fe_2O_3 \cdot nH_2O$$

They should be excluded from charges intended for making quality steels. Used fire bars also contain much sulphur. Sheet materials plated with zinc or tin are not permitted for charging into furnaces.

Scrap of medium size must be charged rapidly, which is most decisive for higher productivity of a furnace operating by the pig-and-scrap process where the charging and melting take up more than half the tap-to-tap time.

Pig iron composition. Pig iron melts more quickly than scrap and accelerates melting of the latter. The melting period and therefore tap-to-tap time are shortened even more when liquid pig iron is used (e.g. from a cupola furnace). The hotter the run of the furnace, the less pig iron is needed in the charge to obtain the specified carbon content on meltdown.

During the charging and melting the impurities of the charge are oxidized. The longer the periods of charging and melting, the more is the oxidation of iron and carbon. The oxidation loss of carbon during charging and melting is 30-40 per cent on the average; this must be taken into account in charge calculations.

The carbon content of the melt by the moment of meltdown must be 0.4-0.7 per cent above that specified for the final steel. This is needed for further oxidation during boiling to heat up the bath to the required temperature and ensure conditions for the removal of gases and nonmetallic inclusions from the metal.

Let us calculate, for instance, the amount of pig iron to be charged to make steel with 0.4 per cent carbon. The bath must have 0.9 per cent C by the moment of meltdown (to make a surplus for the boiling period). Taking the loss of carbon during the charging and melting as 40 per cent, the charge must contain 0.9 : 0.6 = 1.5 per cent C. Assuming the average carbon content of pig iron to be 4 per cent and that of scrap 0.2 per cent, and denoting the amount of pig iron by x and that of scrap by $(100 - x)$, we have

$$4x + 0.2(100 - x) = 1.5 \cdot 100; \quad x = 34.2$$

Therefore, to make this grade of medium-carbon steel, the charge must be composed of 34.2 per cent pig iron and 65.8 per cent steel scrap.

The pig iron must contain not more than 0.2 per cent P, 0.05 per cent S, 1.0-1.5 per cent Si, and 1.0-1.5 per cent Mn. Although the heat produced through exothermic reactions in the furnace operated by the pig-and-scrap process is not very high, but silicon and manganese prevent carbon against oxidation during melting.

The pig-and-scrap process with cold charge. As has been indicated earlier, the charge is calculated so as to introduce a small amount of iron ore (under 2 per cent) during the heat in order to facilitate dephosphorization and the formation of new slag.

It often happens, however, that the metal on meltdown has an extremely high or, on the contrary, an extremely low carbon content. In the first case either the amount of ore added may exceed 2 or 3 per cent of the charge, or the carbon content is controlled by direct oxidation of the bath with oxygen.

In the second case (low melt) the furnace productivity lowers considerably. This is remedied by adding pig iron or mirror iron to the bath.

The whole period of the heat consists of the following successive stages: (1) fettling; (2) charging and melting; (3) boiling; and (4) deoxidizing.

Fettling. According to the experience of advanced steel-melters, it is advisable to begin fettling of the jambs and rear wall already before tapping and continue it as the jambs are being exposed, without waiting until the furnace is tapped completely. The thermal load of the furnace during fettling should be maintained at 70 to 80 per cent of the maximum.

Charging and melting. Since charging and melting take up two-thirds to three-quarters of the total tap-to-tap time, they must be carried out as quickly as possible.

The sequence in which components of the charge are fed into the furnace has a great effect on the rate of melting. It is advisable that the first batch of the charge placed on the hearth should consist of small-size clean scrap amounting to 10-25 per cent of the total scrap specified. Limestone should never be laid first on the bottom since it chills and blocks the hearth and, moreover, delays the formation of normal slag.

Boiling (*refining and finishing*). After meltdown the initial ferruginous slag is skimmed off during the dephosphorization if the phosphorus content of the final steel is not to exceed 0.03 per cent.

Slag basicity must be 1.7-2.0 by the moment of slagging-off, and the bath should be well heated. The furnace is loaded with at least 8 kg dry iron ore per ton of charge in order to accelerate oxidation of phosphorus and its passage to the slag; then, after a short period, fuel supply is reduced to facilitate foaming and skimming of the slag.

After slagging-off, a new slag of normal basicity is formed by simultaneously adding lime and bauxite (or fluorspar), so that it contains at least 40 per cent CaO and not more than 18 per cent SiO_2. An excessively thick slag can be thinned and made fluid by adding bauxite, fluorspar, or broken fireclay brick. The addition of bauxite must be stopped at least 40 minutes before preliminary deoxidation. Slag basicity by the end of this period should be as high as 2.2-3.5.

When the slag contains at least 12 per cent FeO and 40 per cent CaO and not more than 12-18 per cent SiO_2, and the temperature is high enough to make it fluid, the phosphorus content of the metal can be lowered very quickly. The temperature of the bath must be such as to ensure intense boiling with evolution of small bubbles. The bath is then refined from nonmetallic inclusions and gases.

Deoxidizing and alloying. When making killed steels, wide use is made of preliminary deoxidation which is aimed at reducing the content of nonmetallic inclusions in steel. An adequate time interval is allowed between this stage and the final deoxidation so as to let the oxidation products float up to the slag and also minimize the loss of the ferro-alloys to be introduced later.

This preliminary deoxidation begins after the carbon content of the bath has dropped down to the specified limit. Best results are obtained by using ferro-alloys of the complex type, for instance, silico-manganese. The amount of silico-manganese to be added is calculated so as to introduce 0.10-0.17 per cent Si into the bath.

If complex ferro-alloys are not available, ferro-manganese is used for preliminary deoxidation (calculated so as to bring the manganese content of the metal to its lower limit); eight or ten minutes later ferro-silicon heated up to 600-700°C is added (so as to introduce 0.10-0.17 per cent Si into the bath). This sequence of operations is observed to obtain better purity of steel. The final deoxidation and finishing to the specified composition are carried out in the ladle.

The course of the pig-and-scrap process in oil-fired furnaces is illustrated by the graphs in Figs. 101 and 102. The heats concerned were made in normal conditions using oxygen to intensify fuel oil combustion.

The pig-and-scrap process with hot charge. The time required in the pig-and-scrap process for charging and melting can be substantially reduced if liquid pig iron (hot metal) is used. It is poured onto layers of scrap and limestone that have been heated up to a temperature above the melting point of iron (to prevent chilling of the bath). If liquid iron is not available, a supply can be provided by melting iron pigs and iron scrap in cupola furnaces, i.e., by producing synthetic iron.

The use of liquid iron from cupola furnaces, when properly organized, provides certain advantages and a high yield of liquid steel, often as much as 94-95 per cent of the metallic charge.

But the synthetic iron obtained from coke-fired cupolas usually has a high sulphur content, and its desulphurization in the ladle entails extra expenses and excessive cooling (by 100-140°C).

The Rote Erde Works in Aachen (FRG) employs a duplex process (cupola and basic open-hearth furnace) with seven open-hearth furnaces of a capacity of 30-50 tons using liquid iron with 1 per cent Si melted in cupolas.

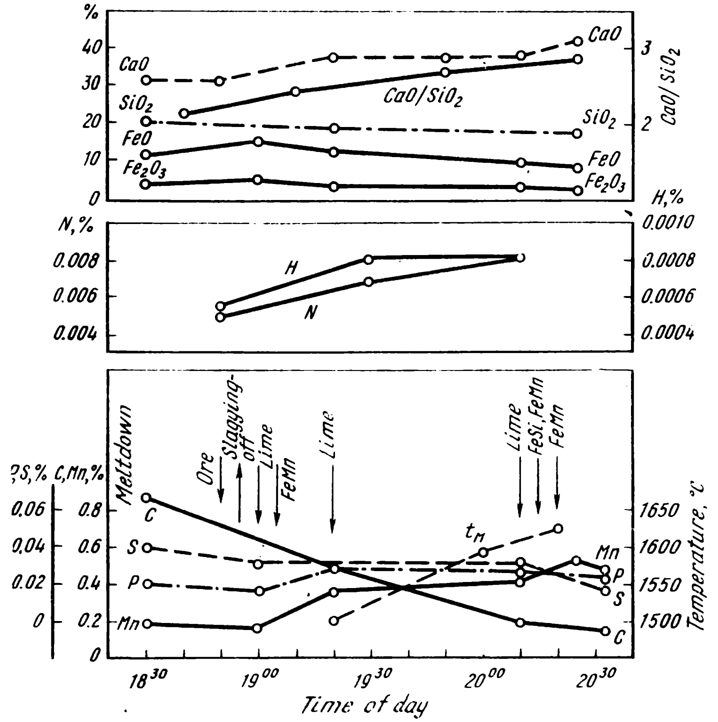


Fig. 101. Variations of inclusions and components in slag during the ordinary pig-and-scrap heat

Before charging pig iron, scrap is heated up in the furnaces to 1300°C. The process shortens the tap-to-tap time and increases the yield of steel up to 94 per cent of the metallic charge. Despite these obvious benefits, the process has not found wide application because the iron produced in coke-fired cupolas becomes rich in sulphur, and also because it is difficult to coordinate the operation of cupolas and open-hearth furnaces.

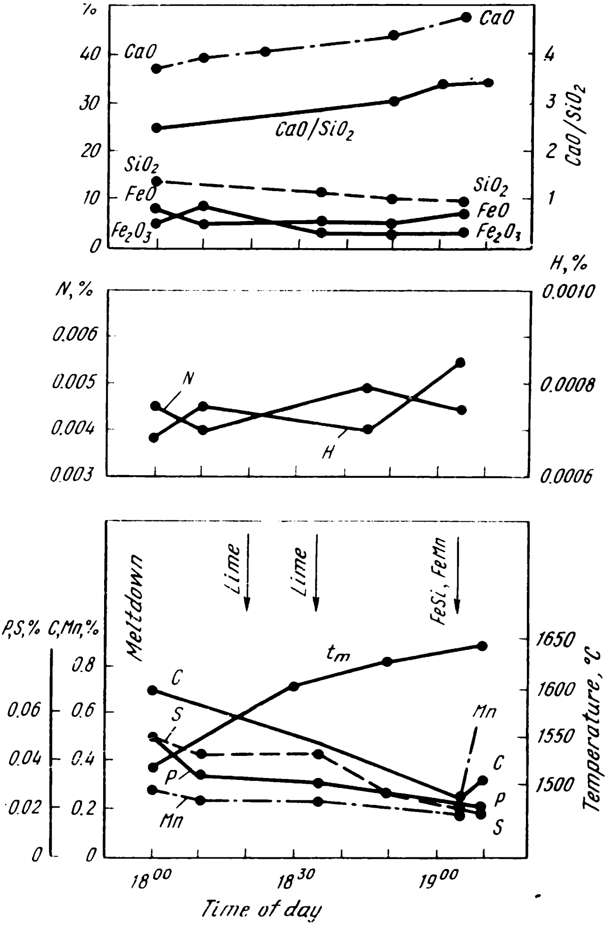


Fig. 102. Variations of slag inclusions and components during the pig-and-scrap process with oxygen being fed to the flame

These disadvantages have been removed in recent years by using basic-lined cupolas and hot blast. The blast air is heated up by firing part of the cupola gas (17-22 per cent CO, 2 per cent H_2, and 8-12 per cent CO_2) preheated to 500°C in recuperators. The gas, taken off from the cupola at a level 600-1000 mm below the charging apparatus, is directed into a cyclone dust collector and then into a recuperator. Natural gas can also be used for firing cupolas.

The use of recuperators makes it possible to raise the temperature of blast and thus to produce liquid iron with a temperature of 1500-1520°C on tapping. With such a high-temperature mode of operation, desulphurization of iron in the cupola is made by a slag of a basicity of 2.0-2.5. This obviates the treatment of iron in the ladle with soda, even when the charge is composed of low-grade steel scrap.

With a charge consisting of steel scrap, 20 per cent coke, and 6-12 per cent limestone, the synthetic iron produced contains 3 per cent C or more and 0.1-0.3 per cent Si (owing to the addition of 45-per cent ferro-silicon).

As has been shown in practice, it is expedient to operate the cupola furnace continuously and accumulate the iron produced in a mixer; this solves the problem of coordinating the operation of cupolas and open-hearth furnaces.The process can be improved further by employing cupola furnaces blown with hotter air (925°C) and a charge composed of 100 per cent scrap and turnings. The cupola-open-hearth furnace duplex process has found application in a number of countries; more recently, a hot-blast cupola furnace-oxygen converter duplex process has also come into use.

Carbonization of the liquid bath. The composition of the charge for the pig-and-scrap process cannot be determined precisely on account of the difficulties in determining the carbon content of purchased scrap and also of some other factors. Because of this the content of carbon in the molten bath must sometimes be increased by charging pigs of conversion iron or mirror iron. But the use of more pig iron in the charge increases the cost of steel. Another, less expensive method of carbonization of the metal is employed at present by blowing carbon-containing materials (Table 40) in the metal by means of a jet of compressed air or nitrogen. Experiments have shown that this method ensures

Table 10

Carbon-containing Materials (carburizers)

Material	Composition of dry substance at 105°C					Moisture content at 105°C, %	Ash content, %
	C	SiO_2	S	H_2	N_2		
Graphite . . .	98.8	—	0.1	—	—	0.2	1.0
Coal	90.5	2.9	1.1	0.9	1.0	2.0	5.4
Anthracite . .	90.5	—	1.0	0.9	1.0	—	4.3
Coke	85.5	3.5	0.8	0.8	0.7	1.0	8.2
Coal dust . . .	69.8	—	0.5	—	—	1.5	13.3

a rapid rise of the carbon content in the bath owing to mixing of the metal by the blown-in carburizer.

The degree of utilization of the carburizer may be different depending on its properties, temperature of the bath, carbon concentration in the bath at the beginning of carbonization (i.e., the degree of oxidation of the bath), the flow rate of carburizer and its particle size. A part of the carbon is assimilated by the bath, another part acts as a deoxidant and is removed from the bath as CO, and still another part floats up with ashes to the slag and is spent for partial reduction of oxides in the slag.

The effect of particle size of the carburizer on the degree of its utilization may be seen from the following: when anthracite powder with a unit surface area of 8 m^2 per 100 g was used, 61 per cent of its carbon was assimilated by the bath, while in another case, with a coarser powder, having a unit surface area of 1 m^2 per 100 g, the assimilation was only 45 per cent. According to some data, a rise in the temperature of the bath has a positive effect on the assimilation of blown-in carburizers.

Figure 103 shows experimental graphs of the effect of the amount of carburizer on the degree of carbonization of mild and high-carbon steels (the carbon spent for deoxidation is neglected).

The pig-and-scrap process for making technically pure iron. Some industries have a demand for technically pure iron, i.e., a metal very low in impurities, such as 0.02-0.05 per cent C, 0.01-0.07 per cent Si, 0.01-0.08 per cent Mn, 0.006-0.010 per cent P, and 0.008-0.018 per cent S. The process for making technically pure iron may be characterized by the following features:

(1) the thermal load is gradually intensified, so that the bath is heated well above 1600-1620°C, which is possible in furnaces of a high thermal capacity fired with a high-calorific fuel containing no sulphur;

(2) the slag is skimmed off and made anew more than once as the carbon is burnt out and bath temperature raised; this results in that the slag becomes rich in iron and calcium oxides and low in acid oxides and sulphides and the metal is refined of carbon, manganese, sulphur, and phosphorus.

Because of the difficulties connected with removing sulphur, its content must be carefully controlled in the fuel, fettling materials, fluorspar, and other materials in the melt, as well as in the metallic charge.

Bringing carbon content down below 0.06 per cent also presents great difficulty. As has been shown by experiments, the protracted period of removing residual carbon can be substantially shortened by direct oxidation of the bath with oxygen, the blowing of the metal with oxygen being started at a carbon concentration of 0.2-0.3 per cent.

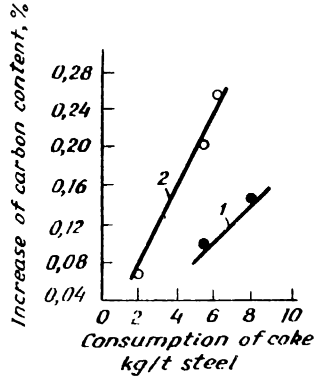


Fig. 103. Curves of carbon content in the bath versus the consumption of carburizer per ton steel

1—high-carbon steel; *2*—medium- and low-carbon steel (Ladyzhensky, Tunkov)

The diagram of a 15-ton heat run by this method (Fig. 104) shows that the rate of carbon oxidation is sufficiently high even with the carbon content below 0.06 per cent. Scrap of strip or sheet iron is sometimes charged into the bath to facilitate the formation of bubbles of carbon monoxide at low carbon concentrations. It has been also observed that

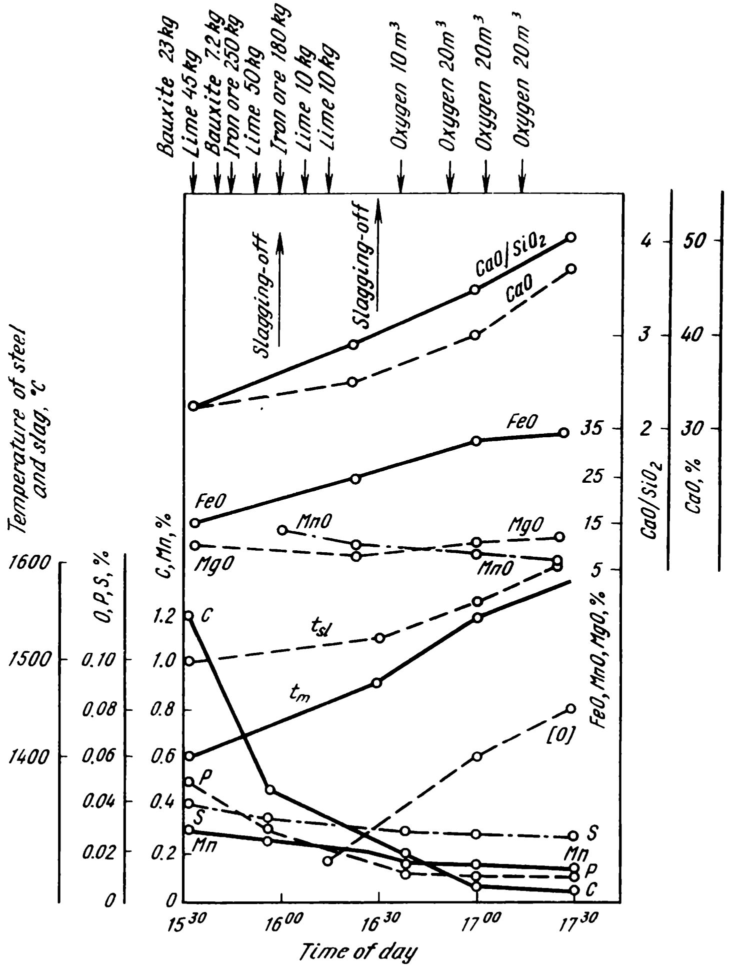


Fig. 104. Graph of a melt for technically pure iron with oxygen blowing of the bath

carbon removal is accompanied with the removal of sulphur from the metal.

Technically pure steel is usually classed as rimming, though it is sometimes produced as killed steel. In the latter case it may be deoxidized with Si, Al, Ca, or Zr. Each of these elements has a high deoxidizing power but forms high-melting oxides incapable of coagulating. They must be used in such combinations as to form fusible compounds, e.g. as alloys Si-Al, Ca-Al, Si-Ca-Al, etc. Pure aluminium, however, is often employed in practice, which is introduced into the bath in cans and additionally into the stream of metal in the launder.

A feature characteristic of the physical structure of ingots of technically pure rimming steel are deep-lying honeycomb blow-holes. Certain temperature conditions are required for rolling this steel, since in the temperature range of 800-1000°C it suffers from red shortness. The stresses arising from rolling at low temperatures are removed by annealing.

Technically pure steel is corrosion- and heat-resistant, highly weldable, can be easily painted, tin- or zinc-plated, lends itself well to deep drawing, and possesses high magnetic induction and low coercive force, which makes it suitable for manufacturing radioelectronic devices, etc.

The carburizing (scrap-carbon) process. The scrap-carbon (carburizing) process is regarded as a variant of the pig-and-scrap process resorted to in unfavourable circumstances when there is a partial or complete lack of pig iron for the charge. Carbon is then brought in by adding solid carburizers.

In this process, the charge is harder to melt than in the ordinary pig-and-scrap process, so that a hotter run of the furnace is needed in order not to prolong the melting period beyond reasonable limits. The length of this period, however, can be kept down to normal by using oxygen to intensify combustion.

As the carburizers bring in enough carbon into the charge, the boiling in the carburizing process differs from the ordinary process only in that the slag has a very high basicity.

The product of silicon oxidation, SiO_2, is a necessary component of normal slag; when the slag is low in silicon

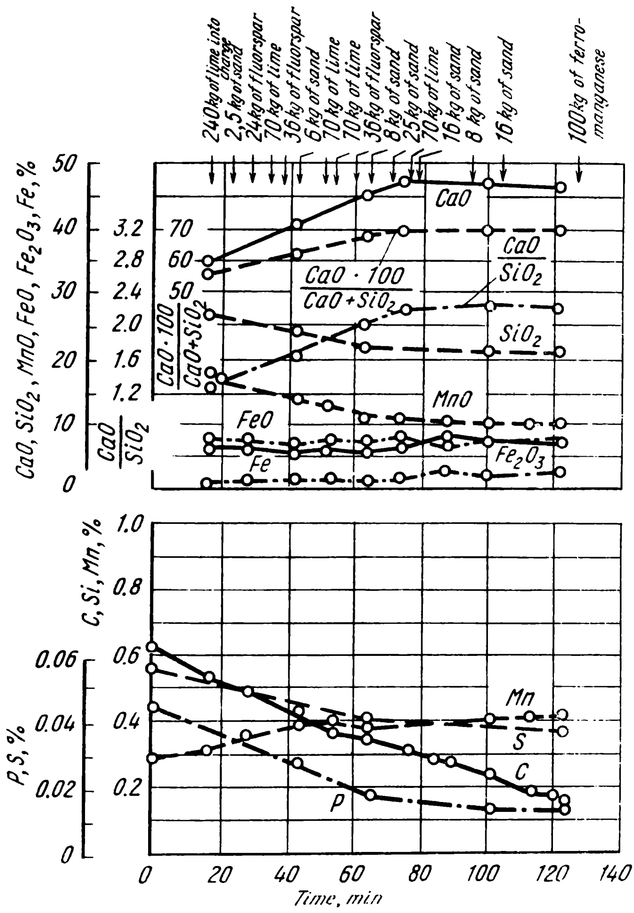


Fig. 105. Variations of the content of inclusions in the bath and of the components of the slag in the carburization process

oxide, its composition is corrected by adding sand (Fig. 105). This reduces somewhat the foaming of slag and improves heating of the bath.

A low manganese content of the charge is remedied by introducing ferro-manganese, mirror iron, or manganese ore. Slagging-off is not required in most cases, since the charge is low in phosphorus and sulphur.

Reduction of manganese is facilitated through floating up of part of the carburizer not picked up by the bath to the slag. For that reason it is advisable to put manganese ore onto the slag, when needed.

The best carburizers are anthracite, graphite, and coke, the last being obtained from coal (with a relatively low sulphur content), peat, pitch or crude petroleum. Charcoal, though beneficially low in ash, burns up very rapidly during charging because of its light weight and some of it floats up to the surface of slag.

When carburizers are being charged, care must be taken that they are not uselessly burnt up in the oxidizing furnace atmosphere; this is prevented by covering them as quickly as possible with layers of scrap.

With good charging, it may be taken that one unit mass of carbon in pig iron requires one or two units of carburizer of the type of coke or anthracite, two or three units of coal, or three or four units of charcoal. The carburizing scrap-carbon process, as practised hitherto (i.e., without intensification with oxygen), reduces the productivity and campaign of furnaces and increases the consumption of fuel and deoxidants. On the other hand, it uses a less expensive charge and causes a lower loss of iron (i.e., increases the yield of steel).

The applicability of the process in normal production conditions has to be solved independently in each particular case.

INTENSIFICATION OF THE PIG-AND-SCRAP PROCESS WITH OXYGEN

As far back as 1926, K.G. Trubin proposed to use oxygen as the atomizer for fuel oil in the burners of open-hearth furnaces in order to raise the theoretical temperature of combustion, which is defined by the formula

$$t_{th} = \frac{Q_{ch} + Q_{s\text{-}f} + Q_{s\text{-}a} - Q_{dis}}{v c_p}$$

where Q_{ch} = chemical heat of fuel
$Q_{s\text{-}f}$ = physical heat of fuel heated up in regenerators
$Q_{s\text{-}a}$ = physical heat of air heated up in regenerators
Q_{dis} = heat lost through dissociation of triatomic gases (CO_2, H_2O)
v = unit volume of combustion products for a given grade of fuel
c_p = specific heat of combustion products

As will be seen from the formula, the theoretical flame temperature of a fuel can be increased by increasing the degree of heating of the fuel and air before their mixing. Another way is to reduce the volume and specific heat of combustion products per unit of the fuel burned.

But the theoretical flame temperature can also be increased artificially, for instance, by using oxygen-enriched air (up to 27-30 per cent O_2) instead of atmospheric air; this will diminish the content of ballast nitrogen and therefore the volume of combustion products. Indeed, when fuel is burnt in common air, the latter brings in 3.762 volume units of nitrogen per unit volume of oxygen contained in the air; this nitrogen is a ballast, since it does not participate in combustion, but is heated up to the flame temperature and thus absorbs some heat.

When oxygen-enriched air is used, the amount of ballast nitrogen is lower and therefore the volume of combustion products is also lower, while the heat evolved through combustion of the fuel is the same as in the former case. But since less heat is spent to heat up the combustion products, the theoretical temperature of combustion and flame temperature will be higher.

The course of a steelmaking process, especially of the pig-and-scrap process, depends largely on heat transfer by radiation from the flame to charge materials during charging and melting. Triatomic gases such as CO_2, H_2O, and SO_2 possess the highest emissivity (i.e., ability to radiate heat). Diatomic gases (H_2, CO, O_2, N_2) are also capable of radiating heat, but only insignificantly and their radiation is usually neglected in calculations.

The products of combustion always contain CO_2 and H_2O, their sum sometimes reaching 30 per cent, which makes the flame luminous. Luminosity, in turn, determines the emissivity. The emissivity of an absolutely black body, C_0 is 4.96 kcal/m^2·h·°K^4. But perfectly black bodies are non-existent in nature. For that reason, the concept of a grey body is used, i.e., the emissivity of a black body is multiplied by its luminosity ε. Thus, the effective emissivity of a grey body is $C = \varepsilon C_0$.

The equation of the Stefan-Boltzmann law for the general case of radiant heat exchange between two surfaces is of the form

$$Q = C\left[\left(\frac{T_f}{100}\right)^4 - \left(\frac{T_c}{100}\right)^4\right] F, \text{ kcal/m}^2\cdot\text{h}$$

where C = effective emissivity of a grey body
T_f = effective conditional flame temperature, °K
T_c = averaged temperature of the heat-absorbing surface (cold materials)
F = surface area, m^2

As will be seen from the formula, the flame temperature is of high importance since the amount of heat transferred per unit area of the bath (or of non-melted scrap) is proportional to the difference between the fourth powers of the temperatures of the flame and of the cold materials and also to the luminosity of the flame. With a good fuel, the luminosity of the flame practically is 0.35-0.55. With an oxygen-enriched flame, the concentration of CO_2 and H_2O increases owing to a lower content of nitrogen, which results in a higher luminosity of the flame. It should be noted, however, that luminosity depends in many cases not only on the presence of CO_2 and H_2O in the flame, but also on the large amount of fine particles of carbon black formed through decomposition of hydrocarbons.

Thus, the pig-and-scrap process can be intensified by supplying oxygen to the flame. But, as has been established by experience, enrichment of air with oxygen is only effective up to approximately 28 per cent (Fig. 106); the curve of the theoretical flame temperature then rises steeply, while with a further increase of oxygen in the air the curve becomes smoother, which is linked with that much heat is lost for the decomposition of CO_2 and H_2O. The further enrichment with oxygen, though giving some effect, is economically unwarranted. For that reason most steelmaking works use air enriched with oxygen maximally up to 24-29 per cent.

It is generally accepted that the heat transfer in open-hearth furnaces is mainly due to radiation, but as the gas velocity at the bath surface in modern furnaces is very high, the proportion of heat transferred by convection can reach 40 per cent at the root of the flame and therefore this kind of heat must also be considered in calculations.

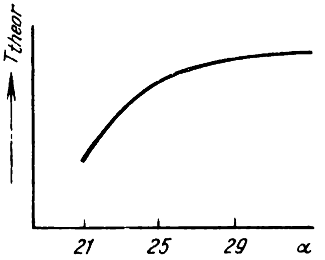


Fig. 106. Theoretical flame temperature against the degree of enrichment of air with oxygen

With oxygen supplied to the flame, the oxidizing power of a furnace, which is determined by the amount of oxygen (kg/h) picked up by the metal from the gases passing through the slag, increases three or four times. For instance, for the same surface area of the hearth and with the common flame the bath absorbs 406 kg oxygen per hour and with the flame enriched to 28 per cent oxygen, 1717 kg oxygen.

In modern practice the method of intensification of combustion by supplying oxygen through burners is widely employed, oxygen being supplied only during the periods of charging and melting. This shortens appreciably the time of melting, speeds up slag formation, and promotes the removal of phosphorus and sulphur from the metal. A drawback of the method is a relatively high consumption of oxygen (15-25 m^3/ton steel).

Cutting of scrap with oxygen jets. This method of using oxygen serves the same purpose of accelerating melting-down of the charge by cutting up scrap (heated up to approximately 1400°C) into smaller pieces by means of jets of oxygen in the reaction chamber. The method has not found wide application since it causes damage to the furnace lining and therefore leads to more frequent repairs of the reaction chamber. The cutting of scrap with oxygen entails the formation of a large volume of vapours of iron oxides, which block the checkers and slag their upper layers as well as have a detrimental effect on the lining of the reaction chamber. A high oxidation loss of iron results in a lower yield of steel and frequently in a 'soft' melt, i.e., an excessively low content of carbon in the metal on meltdown.

Direct oxidation of the liquid bath with oxygen. Gaseous oxygen is introduced into the liquid bath of an open-hearth furnace to accelerate the oxidation of impurities, especially carbon. The method is effective when it is needed to correct the process with the bath being cold or containing too much carbon or when making low-carbon steels (especially of the type of technically pure iron).

With an appropriate rate of oxygen blowing, the rate of oxidation of carbon is two or three times that in the common processes. The bath is heated up quickly. For instance, with 1 per cent O_2 of the mass of the charge introduced into the bath its temperature increases at least by 20°C.

As has been found by the author in his studies of oxidation of carbon, the course of this reaction depends largely on the presence of a gaseous phase at whose boundary the formation of CO bubbles is made possible. When oxygen is being blown into the bath, a tremendous number of bubbles of the active gas are formed. It is this phenomenon that ensures high rates of carbon oxidation. This can be explained by the fact that oxygen bubbles are immediately formed on blowing the bath with oxygen, so that the partial pressure of carbon, p_{CO}, is substantially lower than in heats without oxygen blowing and equals $p_{CO} = p_{at} + \gamma_m h_m + \gamma_{sl} h_{sl}$. As will be seen from the formula, it has no term that would account for the capillary pressure $2\sigma/r$. In addition, the sum $h_m + h_{sl}$ is also smaller in this case, since oxygen is blown into the bath at the metal-slag interface. Thus, the zone of the reaction of carbon oxidation on the surface of numerous oxygen bubbles is located in the upper layers of the bath.

The method of direct oxidation has been found effective for dephosphorization by slagging off the initial ferruginous slags. The intense bubbling and consequently an increased surface of contact between the metal and slag promote rapid oxidation of phosphorus and sulphur, reduce gas saturation of the bath, and favour coagulation and floating up of non-metallic inclusions.

But blowing of the bath with oxygen causes excessive oxidation of iron. Vapours, dust, solid particles of oxides, and splashes of slag damage the furnace lining and rapidly block up the checkerwork. It may be taken that the life of the main roof (which is not affected when oxygen is given to the flame) is reduced roughly by 20-30 per cent when oxygen is used for cutting scrap or for direct oxidation.

The formation of fumes, dust, and splashes, which are carried out with the waste gases or picked up by the lining, results in a noticeably lower yield of metal (by 0.5-1.5 per cent). The composition of the dust in waste gases is approximately as follows: 80-86 per cent Fe_2O_3, 1.18-2.56 per cent SiO_2, 0.30-1.43 per cent CaO, 0.3-0.7 per cent Mn, 1.10-1.64 per cent S, 0.23-1.92 per cent Al_2O_3, and 0.63-0.97 per cent P_2O_5, i.e., the main component of the dust is Fe_2O_3. The size of solid particles suspended in them may be as large as two microns, so that dust-collecting means become indispensable.

The combined method of using oxygen. Simultaneous employment of all these methods, termed the combined method, has proved most efficient in practice. The use of this method in a silica-roof furnace with oxygen enrichment of the flame (to 26-27 per cent O_2) and with speeded-up charging yields a rise in furnace productivity of 22-48 per cent and a reduction of fuel oil consumption by 20 per cent on the average, the consumption of oxygen being 32.5 m^3 per ton steel. By replacing silica roof with chrome-magnesite roof and enriching the air for combustion to 28-30 per cent O_2 during the periods of charging and melting, the furnace productivity is raised by 40-60 per cent and the unit consumption of fuel lowered roughly by 20-30 per cent.

In the former technique of introducing oxygen, this was supplied to the bath at a pressure of 5-10 at through steel pipes 0.5-1.5 inches in diameter. The life of pipes was then lengthened by using protective coatings or refractory lining. It was later suggested to use a water-cooled nozzle with its end placed 75-150 mm above the bath surface. These nozzles, which were usually introduced through the charging doors, are now replaced by single- or multi-nozzles lances passed through the rear wall or the roof into the furnace. The lances are made from seamless tubes and provided with a copper end piece, and are usually water cooled.

In experiments to determine the role of the physical factor (bubbling of the bath) and the chemical one (carbon-oxygen reaction), the bath was blown with the gases of a composition ranging from pure oxygen to pure nitrogen as follows: 100 per cent O_2; 90 per cent O_2; 70 per cent O_2; 44 per cent O_2; compressor air; and 100 per cent N_2. It was found that with any of these gas compositions the removal of carbon was accelerated, even when pure nitrogen was used. But as the oxygen concentration in the gas was increased, i.e., as the physical factor (bubbling) was supported by the chemical one, the rate of decarbonization grew faster.

The scrap-and-ore process with slagging-off. The pig iron for the process is stored in an inactive mixer of cylindrical shape. The mixer cannot be used for carrying out the preliminary reactions by forming an active slag, since that would cause rapid wear of its lining, while its construction makes it impossible to carry out current repairs of the lining. The only reaction that occurs in the mixer is

$$FeS + Mn \rightarrow MnS + Fe$$

The slag is formed in an inactive mixer from its own eroded lining and that of the ladles, from the blast-furnace slag brought in with the pig iron, and from the products of the oxidation of pig-iron impurities occurring in the mixer itself. The composition of the mixer slag may be as follows: 18-35 per cent SiO_2, 2.5-5.0 per cent Al_2O_3, 3.0-7.0 per cent CaO, 0.2-1.0 per cent MgO, 0-25 per cent FeO, 17-40 per cent MnO, and 7-32 per cent MnS.

Measures must be taken to ensure that the mixer slag is not brought into the open-hearth bath. The slags must be skimmed off from the mixer, though it is rather difficult to do this due to their high viscosity, which is aggravated by the presence of graphite ('skulls') and coke breeze that get into the mixer from iron-carrying ladles. Special machines for skimming off the slag have been designed. In this connection other methods of desulphurization of pig iron are therefore of prime importance, either in the blast furnace itself or outside it, e.g. by treating pig iron with soda in the ladle or by one of the more recent methods. A modern mixer of the movable type (mixer ladle) is shown in Fig. 107. Mixer ladles can be used for transporting pig iron both within the works and along common railways to other cities and even other countries. For instance, 300- and 600-ton mixer ladles are employed in Belgium to deliver pig iron from France and the FRG to distances up to 200-300 km. Pig iron can be kept in such a mixer for a long time, since its temperature falls by only 4-5°C per hour.

In the USSR, 420-ton mixer ladles are used with success at the West-Siberian iron and steel works. The pig iron delivered in them to steelmaking shops has a higher temperature and the loss with scrap is lower than with inactive mixers.

In integrated works it is good economics to run open-hearth furnaces with a high proportion of pig iron (55-75 per cent) in the charge, the remainder being scrap. The oxidation of impurities in the bath is forced by adding rich iron ore, i.e., by employing the technique of the scrap-and-ore process.

Charging procedure. The formation of active dephosphorizing slags depends very much on the sequence of charging the solid components (prior to pouring pig iron). The hearth is first covered with a layer of small-size scrap (trimmings) in order to protect it against damage, then limestone and iron ore are charged, and finally large-size scrap is loaded. The practice of charging limestone directly on the hearth (in order to prevent its skulling) is now abandoned.

The amounts of iron ore and limestone to be charged to ensure the specified carbon content of the metal on melt-down and the formation of active dephosphorizing slags of suitable viscosity are calculated from nomograms constructed with due regard for the content of impurities (C, Si, Mn, and P) in the pig iron, for the Fe_2O_3 and SiO_2 concentrations in the ore, and CaO and SiO_2 in the limestone.

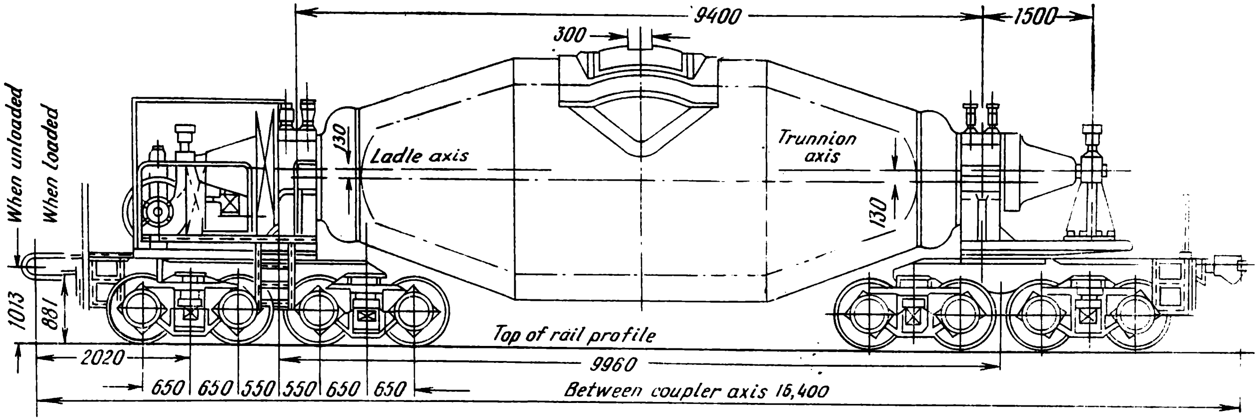


Fig. 107. Mixer ladle

All the pig iron must be poured without interruption onto a well heated charge after fettling the door sills.

The solid charge is believed to melt in the bath in two stages. At the first stage, which lasts until the temperature of the liquid bath is below the melting point of the solid charge, the latter melts through its carbonization by the pig iron. At the second stage, after the temperature of the scrap has reached that of the liquid bath, the solid component of the charge dissolves in the liquid without being carbonized.

If appropriate thermal conditions have been maintained in the furnace during charging, slag formation after the pouring of iron proceeds vigorously, and quite an active slag is formed rather rapidly. To exclude excessive loss of iron with slag (in the form of FeO and iron beads), slagging-off must not be started earlier than 10-15 minutes after all the pig iron has been poured into the bath. By this time the FeO content of the slag becomes lower. The compositions of slag skimmed off during melting in large open-hearth furnaces are given in Table 41. Slagging-off of this initial

Table 41

Composition of Initial Slags Skimmed off During Melting (percentages)

Process	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	MnO *	P_2O_5
Ordinary scrap-and-ore	23-26	1-3	17-23	2-3	19-24	5-6	7-9	2-3
With oxygen-enriched flame . . .	21-24	1-3	18-24	2-3	24-27	5-7	7-9	2-3
With oxygen supplied to flame and bath	20-23	1-3	20-26	2-4	20-27	5-9	7-9	2-3
Feeding large amounts of oxygen to the bath . .	18-20	1-3	28-36	4-6	20-26	8-11	7-9	2-3

* When pig iron contains 15-1.8 per cent Mn, the MnO content of the initial slag may reach 15-20 per cent.

foamy slag to 5 or 6 per cent of the mass of the metal is indispensable in the scrap-and-ore process, since it promotes dephosphorization and desulphurization of the bath and improves heat transfer.

Long before the metallic charge is melted, the bath acquires a temperature high enough to decompose the limestone. The 'lime boil' occurring through the reaction $CaCO_3 \rightarrow CaO + CO_2$ accelerates oxidation of impurities and heating of the bath (through bubbling).

With proper slag control, refining of the melt can be started immediately after meltdown, without losing time on forming a new slag. The time required for refining depends on the composition of the bath on meltdown, slag conditions, and temperature conditions in the bath. It is desirable that the refining period, from meltdown to pure boil, be as short as possible.

The period of pure boil, during which the carbon content of the metal is brought down to the specification, has a decisive effect on the properties of the steel obtained, since vigorous bubbling promotes heating of the bath and removal of non-metallic inclusions and gases from it.

The relatively small amount of the slag left in the furnace can easily be activated by small periodic additions of iron ore (altogether up to 3 per cent of the mass of metal), the slag being skimmed off and its basicity simultaneously increased.

A feature characteristic of this slag is its lower content of iron oxides and a higher basicity compared with the slag skimmed off just after the pouring of pig iron. The composition of this slag may be 19.3 per cent SiO_2, 12.5 per cent FeO, 5.2 per cent Fe_2O_3, 38.3 per cent CaO, 7.6 per cent MnO, 2.6 per cent P_2O_5 and 10.2 per cent MgO. Further removal of sulphur and phosphorus is achieved by increasing the basicity of the final slag.

As an example of the modern scrap-and-ore process with slagging-off, Fig. 108 shows variations in the compositions of the metal and slag during melting of rail steel in a 370-ton open-hearth furnace at the Kuznetsky integrated works. This works was the first to introduce the smelting of low-manganese pig iron (0.45-0.65 per cent Mn) and its conversion into steel, thereby achieving a higher productivity of

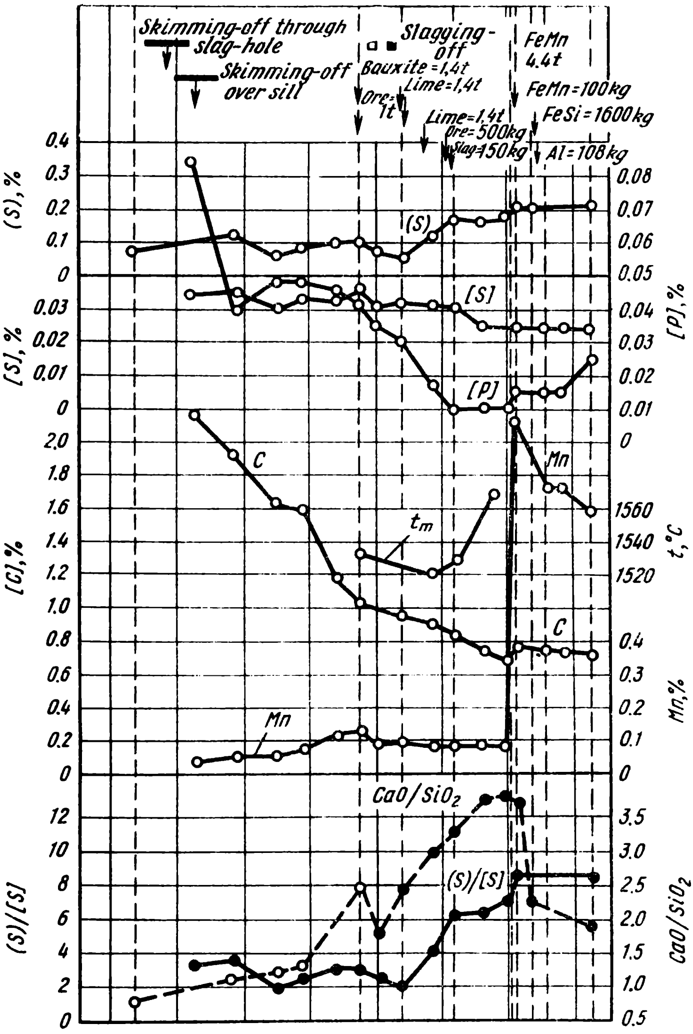
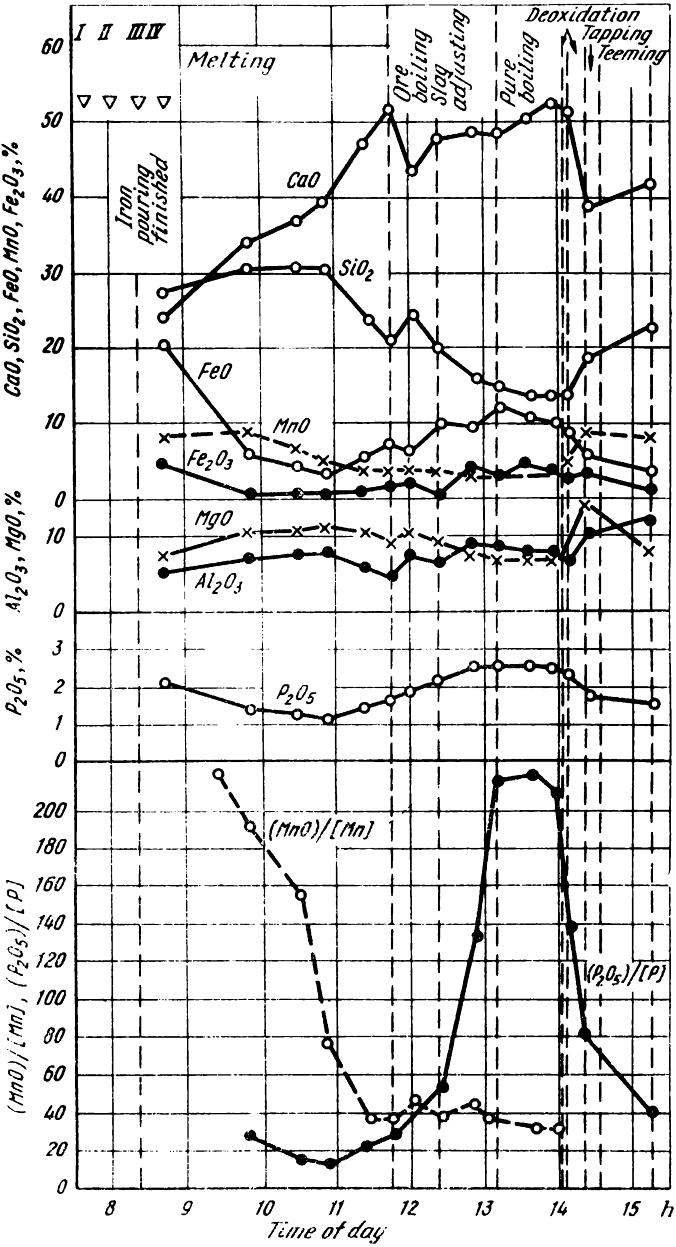


Fig. 108. Graphs of a heat for killed steel by the scrap-and-ore



process in a 370-ton furnace (Kuznetsky Integrated Works) blast furnaces and open-hearth furnaces and lower production costs of pig iron and steel.

As will be seen from the melt diagram, slagging-off begins soon after the pig iron is poured into the furnace. The mass of the slag skimmed off is 25 tons. During that period, intense dephosphorization of the metal occurs in the bath. As follows from the curves, the composition and basicity of the slag vary gradually owing to the passage of lime into the slag solution and the reactions caused by sulphur and manganese in the metal. The material balance of the melt shows that 12 per cent of all the sulphur in the charge is removed with the skimmed-off slag, i.e., the amount of sulphur passed into the slag during melting is not less than in the operation with pig iron of a normal manganese content.

The melt is deoxidized in the furnace with ferro-manganese; in addition, 45-% ferro-silicon and aluminium are introduced into the stream of steel in the launder when it is tapped into two ladles. The coefficient of distribution of sulphur between slag and metal at the end of the heat is quite acceptable for the open-hearth process, which may be explained by a sufficiently high concentration of CaO in the slag. Since the furnace is run without using oxygen, the rate of refining of the bath may be considered satisfactory.

As is evident from the analysis of slag conditions, dephosphorization in the scrap-and-ore process occurs in the initial stage under the action of ferruginous slags, with the formation of mainly $(FeO)_3P_2O_5$ and of some $(CaO)_3P_2O_5$ and $(CaO)_4P_2O_5$, an appreciable part of which is skimmed off; in the final stage, dephosphorization is mainly due to the addition of lime, with $(CaO)_3P_2O_5$ and $(CaO)_4P_2O_5$ being formed.

Making Cr-Ni-Mo *steel by the scrap-and-ore process.* The steel was made in a 350-ton open-hearth furnace from a charge composed of 72 per cent hot metal and 28 per cent scrap, without using oxygen, by the following process.

The slag was skimmed off through the slag hole in the rear wall of the furnace and over the still of the central charging door during the first half of the melting period, the total volume of the skimmed-off slag being 2.5 slag ladles.

High activity of the slag was maintained by adding iron ore three times during the period. New slag was formed by adding lime, bauxite, and iron ore. Alloying with nickel and molybdenum was done after dephosphorization.

Indices of the scrap-and-ore process with slagging-off. The total amount of slag skimmed off comes to 8-9 per cent of the mass of metal, and 5-6 per cent usually remains in the bath on meltdown. The operation of slagging-off has certain advantages and drawbacks. Its advantages are a smaller thickness of the slag layer and correspondingly shorter length of the heat, and also a smaller amount of CaO consumed in the subsequent periods of the heat since a substantial amount of SiO_2 and P_2O_5 is removed together with the slag from the bath.

A drawback is a high loss of manganese with the slag, resulting in the bath having on meltdown a reduced content of manganese (only 0.15 per cent and often as low as 0.08-0.12 per cent instead of 0.2-0.3 per cent in the process without slagging-off). Another drawback is a high loss of iron with the slag and consequently reduction of the metal yield by 2 per cent of the mass of the metallic charge, notwithstanding the high degree of reduction of iron from the ore.

Table 42 gives the material and heat balances of a melt in a basic open-hearth furnace run by the scrap-and-ore process, with oxygen being used for refining the bath.

The pig-and-ore process without slagging-off. The high losses of iron in the skimmed slag have led to the conviction that the skimming-off of the initial slag is inexpedient when ordinary low-phosphorus pig iron is to be converted into plain steels.

The process without slagging-off was run with the charge being 100 per cent liquid iron. This was poured into the bath after charging iron ore in an amount of 20 per cent of the mass of the charge and the specified limestone into the furnace and heating them up to a moderate temperature so as not to cause vigorous reactions. Dephosphorization of the metal proceeded well and was finished long before meltdown. The yield of steel in the heats reached 108 per cent, which is indicative of a high degree of reduction of iron and manganese from the slag.

Table 42

Material and Heat Balances of a 500-ton Basic Open-hearth Heat by the Scrap-and-ore Process with Oxygen Used for Metal Refining

A. Material Balance per 100 kg Charge (prior to deoxidation)

Input, kg		Output, kg	
Liquid iron	65.000	Steel	102.864
Steel scrap	35.000	Slag	11.580
Iron ore	13.740	CO from carbon oxidation	6.060
Limestone	4.170	CO_2 from decomposition of limestone	1.453
Lime	1.020	H_2O as moisture in iron ore and limestone	0.356
Fettling materials and roof wear	1.700		
Technical oxygen	0.856		
Oxygen from furnace atmosphere	0.827		
Total	122.313	Total	122.313

B. Heat Balance of Reaction Chamber

Input, %		Output, %	
Physical heat of pig iron	13.50	Enthalpy of:	
Heat of exothermic reactions	19.50	steel	28.20
Heat of slag formation	0.70	slag	5.17
Chemical heat of natural gas and fuel oil	43.00	waste gases	50.77
Physical heat of air	23.30	Heat to decompose limestone, raise the temperature of gases of the charge, and vaporize moisture	4.84
		Heat loss due to radiation and furnace cooling	11.02
Total	100.00	Total	100.00

But the operation of the furnace with a thick layer of slag turned out to be economically inefficient. The furnace productivity was low, the heats lasted long and consumed much fuel, and the final steel was high in sulphur. For these and some other reasons, the process is abandoned in the industry and replaced with the scrap-and-ore process, in which, as is known, the metallic charge includes scrap and the heats are made with slagging-off to speed up desulphurization of the metal.

Thermal effects of the reactions in the scrap-and-ore and pig-and-ore processes. When being heated, limestone begins to decompose noticeably into CaO and CO_2 at 500°C, and decomposition is complete at 900°C.

The decomposition of Fe_2O_3 occurs in the following sequence:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$$

At temperatures of the open-hearth process, Fe_2O_3 cannot be present in free state since the formation of FeO is observed at 200-450°C depending on kind of iron ore, and that of Fe at temperatures around 700°C. The simultaneous charging of limestone and ore into the furnace leads to the formation of chemical compounds $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$, in which Fe_2O_3 acts as an acid oxide.

The formation of these fusible calcium ferrites results in the limestone and iron ore being melted together to form a ferruginous-limy slag of the $CaO \cdot Fe_2O_3$ type on the hearth even before pig iron is poured into the furnace.

The thermal effects of reactions of oxidation of impurities calculated for various conditions of heating the iron ore and lime and for bath temperatures of 1300°C and 1600°C are given in Table 43. By comparing the results obtained it is possible to draw certain conclusions of principal significance for the scrap-and-ore process.

The oxidation of impurities — Si, Mn, and P — in the initial stage of the process is accompanied by liberation of heat if the ore has been preheated.

The introduction of ore and fluxes in the cold state into the liquid bath, either at the beginning of the process or in its final stage, always entails an appreciable absorption of heat.

Table 43

Thermal Effects of Oxidation of Impurities with Iron Ore in a Basic Open-hearth Furnace at Various Temperatures

Element being oxidized	Bath temperature, °C	Ore and flux	Temperature of ore and flux, °C	Thermal effect produced, cal	Thermal effect per unit mass O_2, cal
Si	1300	Fe_2O_3, CaO	0	−13 754	−143
	1600	Fe_2O_3, CaO	0	−118 854	−1240
	1300	Fe_2O_3, CaO	1000	+173 046	+1800
	1300	Fe_2O_3, $CaCO_3$	0	−360 220	−3752
	1600	Fe_2O_3, $CaCO_3$	0	−489 614	−5100
P	1300	Fe_2O_3, CaO	0	−33 271	−139
	1600	Fe_2O_3, CaO	0	−277 591	−1157
	1300	Fe_2O_3, CaO	1000	−393 765	+1640
	1300	Fe_2O_3, $CaCO_3$	0	−726 187	−3020
	1600	Fe_2O_3, $CaCO_3$	0	−1 018 975	−4250
M	1300	Fe_2O_3	0	−7 007	−145
	1600	Fe_2O_3	0	−41 087	−856
	1300	Fe_2O_3	1000	+462 273	+965
C	1300	Fe_2O_3	0	−152 199	−3170
	1300	Fe_2O_3	1000	−98 823	−2060

The oxidation of carbon is also accompanied, in all conditions, by the absorption of an appreciable amount of heat.

It then follows that in the modern practice of operation of open-hearth furnaces by the scrap-and-ore process with liquid pig iron it is economically profitable to preheat iron ore and limestone on the furnace hearth together with scrap before pouring hot metal into the furnace.

INTENSIFICATION OF THE SCRAP-AND-ORE PROCESS WITH OXYGEN

Let us consider the conditions for using oxygen in the scrap-and-ore process which is the main one employed in the world manufacture of steel.

As has been shown by the studies carried out in various countries, the use of oxygen to increase the flame temperature in the scrap-and-ore process not only appreciably reduces the heating time of the melt (i.e., charging + + heating + pouring pig iron + melting), but also the period of carbon oxidation.

We shall take as an example the operation of a 250-ton furnace with 65-70 per cent pig iron in the charge. The fuel is a mixture of coke-oven and blast-furnace gases with a calorific value of 2000-2500 kcal/m^3. The furnace is operated for rimming steel.

With the air enriched to only 25 per cent O_2 and an oxygen consumption of 35 m^3 per ton steel during the heating period, the average tap-to-tap time is approximately 6.0 hours, i.e., approximately 20 per cent shorter than in heats without oxygen. At the same time the unit consumption of fuel is reduced roughly by 20 per cent.

A higher oxygen content of the air (30 per cent) increases the thermal load of the furnace, resulting in further shortening of the tap-to-tap time (by 60 per cent) and reduction of unit fuel consumption (by 35 per cent). The rate of carbon oxidation then reaches 0.9 per cent per hour.

The use of oxygen to intensify combustion in the heating period makes it possible to tap four melts a day from a 250-ton furnace.

A higher rate of carbon removal from the bath under an oxygen-enriched flame is due not only to a higher temperature of the flame itself, but also to the increased oxidation of the flame gases and the slag. The effect produced, however, is substantially lower than that obtained when oxygen is used directly to blow the bath. For that reason the present trend is to cut the supply of oxygen to the flame as soon as pig iron is poured into the bath, further oxygen supply being made only for direct blowing of the metal.

This method of intensifying an open-hearth melt is especially effective when the furnace is run by the scrap-and-ore process with a high proportion of pig iron in the charge. It is considered expedient to begin the blow 15-20 minutes after pouring in the hot metal, at the same time cutting off the supply of oxygen to the flame, i.e., feeding oxygen to the flame only during rapid charging and heating of the solid charge. In many shops the bath is blown with oxygen through a number of multi-nozzle lances in the furnace roof.

When the bath is lanced with oxygen, it is agitated more thoroughly owing to the energy of oxygen jets. The stronger stirring, in turn, increases the rate of carbon oxidation and therefore the rate of pick up of oxygen by the bath from the reaction chamber. Some of the blown oxygen, however, is spent on oxidizing iron and forming ferrous oxide which is partly dissolved in the bath and partly passes to the slag. The lower the carbon concentration of the bath, the more ferrous oxide passes to the slag.

Ways are being sought for in the USSR and other countries to improve the method by blowing large furnaces with oxygen at rates of 6000 to 13,500 m^3/h. Oxygen is fed to the bath according to a graded schedule in order to reduce the loss of iron through oxidation and with beads and skimmed-off slags, since it is iron rather than carbon that oxidizes most intensively until the bath is heated up to 1470°C. During skimming of the initial slag, a 500-600-ton bath is blown at a rate of 3500-4000 m^3/h, later at a rate of 5000-8000 m^3/h, and during the refining period at a rate of 4000-6000 m^3/h. As a result of the oxidation of elements, including iron, a high temperature (around 2400°C) develops in the reaction zone and vaporization of iron and oxides occurs there.

With this technique of running a heat, carbon is oxidized at a very high rate and there is plenty of time to heat the bath above the varying liquidus temperature, which is largely promoted by the afterburning of an appreciable amount of the carbon monoxide evolved from the bath. This makes it possible to reduce the fuel supply to the furnace and thus to minimize the consumption of fuel per ton steel (respectively to 39-30, 88-84, and 72-68 kg for furnaces of the capacity of 250, 500, and 600 tons). The total consumption of oxygen varies within 30-45 m^3/t, 70 per cent of which being blown into the bath. The method ensures high productivity, *viz.* 81-87 t/h, and even 103-109 t/h in forced heats.

A disadvantage of this method is high absolute losses of iron with overflowing and skimmed-off slags. With an intensified supply of oxygen to the bath the content of FeO and Fe_2O_3 in overflowing slags is as high as 32-44 and 4-8 per cent, respectively. The slag is also highly viscous and heterogeneous because of the presence of iron beads. In addition, the loss of iron in the dust that forms during blowing amounts to 4.0 kg per ton steel, compared with 1.0 kg when oxygen is fed to the flame alone. Because of the relatively high losses of iron with beads and iron oxides in the slag, and through the oxidation of impurities, the metal yield is rather low (87-91 per cent).

By using the results of numerous experimental melts, certain empirical formulae have been derived that characterize the principal parameters of processes using large amounts of oxygen for blowing the bath. The rate of carbon oxidation during the period of bath blowing with oxygen can be described by a linear equation which varies but not very noticeably with the number of lances used for oxygen supply:

$$v_C = 0.46 + 0.067I$$

The total concentration of ferrous oxide in skimmed-off slag recalculated for % Fe_2O_3 = 1.35 FeO can be found approximately by the formula

$$\%\Sigma\,(FeO) = 19 + 4I^{0.76}$$

and the rate of heating of the bath during blowing, by the linear equation

$$v_t = 56 + 7.2I$$

where I = intensity of bath blowing with oxygen, $10^3 \cdot m^3/h$
$\%\Sigma(FeO)$ = total content of iron in slag, recalculated to FeO, per cent
v_t = rate of bath heating during blowing, °C/h
v_C = rate of carbon oxidation during the period of blowing, per cent C/h

The intensity of bath blowing with oxygen may be different at various works: low (6-9 $m^3/t \cdot h$), medium (10-15 $m^3/t \cdot h$) or high (18 $m^3/t \cdot h$ and more).

In heats carried out with oxygen enrichment of the flame during the charging period and with bath blowing during subsequent periods, the charging must be speeded up, especially of steel scrap. With the flame enriched to 25-30 per cent oxygen and with bath blowing, the rate of charging for 300- and 600-ton furnaces must be increased respectively to 240 and 360 t/h. Such a high rate can only be ensured if the density of scrap in charging boxes is not less than 2.5 t/m^3.

In heats using large amounts of oxygen, the unit consumption of solid oxidants reduces by 30 per cent and that of limestone by 16-30 per cent compared with common heats without bath blowing.

With such intensified operation of furnaces, the life of their lining reduces by 3-11 per cent on the average and therefore the time of hot and cold repairs increases up to 12 per cent. The life of the furnace roof with bath blowing is roughly 20 per cent shorter than with oxygen supplied to the flame only.

A graph of the process and thermal conditions for a heat run in a 250-ton open-hearth furnace of the Makeevsky works with oxygen blowing of the bath is given in Fig. 109. It presents the main data on carbon oxidation and the rate of heating of the bath, and also on oxygen consumption. The latter is 42.2 m^3 per ton steel, of which 32.6 m^3/t is spent on blowing the bath and 9.6 m^3/t fed to the flame.

With an increase of unit oxygen consumption, less ore and flux are required for a heat so that the amount of slag is reduced and less iron is consequently lost in the overflowing and skimmed-off slags.

The slag skimmed off from the bath amounts to two-thirds of the total slag formed in the furnace. To reduce the loss of iron with it, skimming-off should be delayed for a certain time until the slag becomes low in ferrous oxide through oxidation of carbon, which occurs at a high rate.

Such heats are especially favourable in forming slags of an appropriate basicity. Rapid dissolution of the lime in the slag is promoted by a high concentration of ferrous oxide.

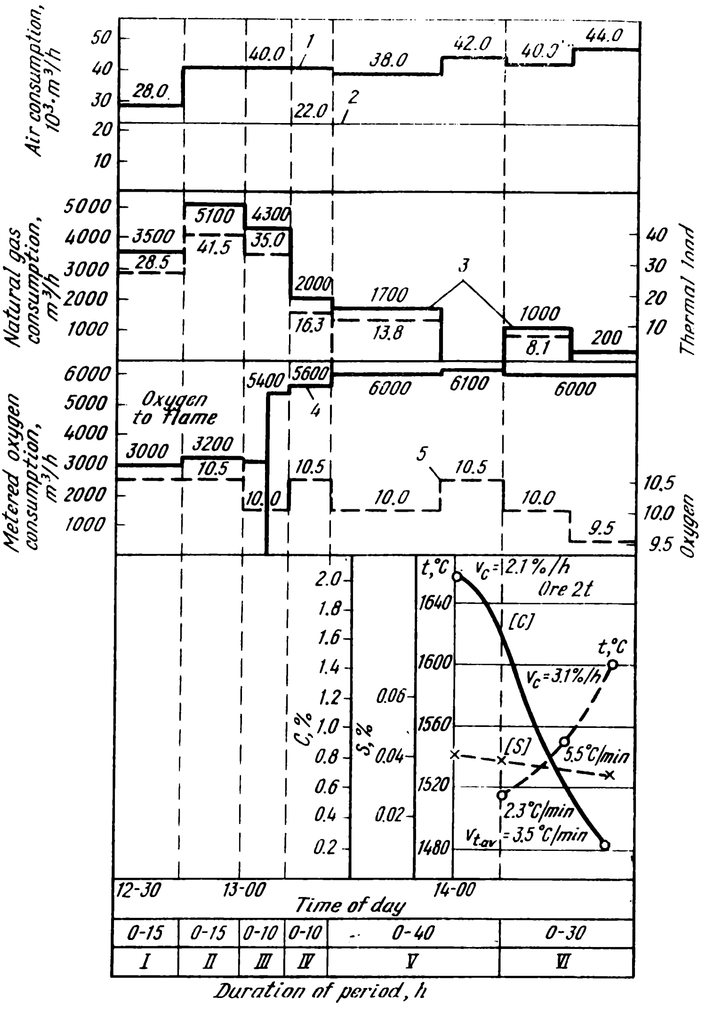


Fig. 109. Graphs of the thermal and process conditions of a heat by the scrap-and-ore process with intensive oxygen blowing of the bath

I—fettling; *II*—charging; *III*—heating; *IV*—pouring of iron; *V*—melting; *VI*—refining; *1*—primary air; *2*—secondary air; *3*—natural gas; *4*—oxygen to the bath; *5*—oxygen pressure

Special attention must be paid to the supply of oxygen to the bath during the melting period so that its rate of feeding may be increased only by the moment when the bath is well heated up and the reaction of carbon oxidation can proceed actively. It has been found that a high rate of carbon removal from the metal is unattainable in the earlier stage of the melting period until the bath is heated to 1470-1480°C, irrespective of the rate of oxygen supply to the bath, since the scrap is not yet fully melted down. Because of that the oxygen fed to the bath soon after iron pouring is mainly consumed on oxidizing silicon, manganese, and phosphorus, and partly on oxidizing iron. To reduce the loss of iron through oxidation and with slag and dust, it is therefore important to blow the bath during the melting period according to a graded schedule. With such a high rate of oxygen consumption (32.6 m^3/t), the rate of heating of the bath reaches 160-200°C/h.

The dust content of the waste gases varies from 8 g/m^3 with an oxygen supply of 1800 m^3/h to 26-40 g/m^3 at 8000 m^3/h, and even higher with a stronger supply.

The amount of dust depends on the location of oxygen lances (in the metal, in the slag, or at the slag-metal interface), the number of nozzles, the level of slag in the bath, etc., less dust being formed when the lance is set at the slag-metal interface or immersed into the metal. Reduction in the oxygen content of the blow mixture to 75 per cent results in less dust being formed since the temperature of the metal in the local zone is reduced. Still less dust is formed when the bath is blown with air.

It has been found that the period of maximum dust formation coincides with that of maximum decarbonization of the bath, which reaches a rate of 1.8-2.2 per cent C per hour. For the scrap-and-ore process with 70 per cent of hot metal in the charge, this period is observed at a carbon concentration of 1.2-2.3 per cent in the bath.

The more intense dust formation during the maximum decarbonization may be explained by the additional oxidizing action of carbon dioxide on iron vapours by the reaction

$$CO_2 + Fe_g = FeO_{vap} + CO$$

Carbon dioxide will interact with iron in the reaction zone by the reaction

$$CO_2 + Fe_l = FeO_l + CO$$

and, when the equilibrium value is exceeded, by the reaction

$$CO_2 + C = 2CO$$

But if the diffusion of carbon from the depth of the metal to the surface of the reaction zone is low, then iron will be oxidized:

$$CO_2 + Fe_l = FeO_l + CO$$

It then follows that the use of oxygen can provide a substantial reduction of the tap-to-tap time through more rapid oxidation of carbon and more rapid heating, and therefore a lower unit consumption of fuel and higher productivity. But this can only be realized with proper organization and equipment, *viz.* rapid charging at a rate of 250-360 t/h, sufficiently intensive blowing of the bath with oxygen during the right time, use of high-resistant refractories in the lining of the furnace, rapid hot and cold repairs, proper removal of slag from the slag pockets and the bottom of the regenerators, and elimination of bottle-necks in all departments of the shop.

In order to lengthen the furnace life, it is advisable to build the main roof higher and to use guniting on a large scale for repairing the roof and walls. Slag ladles must be swiftly replaced to cope with the large volume of overrunning and skimmed-off slags. The checkerwork of the regenerators must be periodically blown with air and washed with water at high pressure. Waste gases must be properly cleaned to reduce their dust content to an admissible level.

It must also be studied whether it is more economic to force one or two furnaces in the shop or to transfer a certain number to forced operation and keep the rest in reserve. These problems must be solved in advance, since experience shows that when a furnace is being forced in a shop, this often causes difficulties in planning the work of the shop as a whole.

Steelmaking in a twin-bath furnace. As mentioned earlier, much carbon monoxide is evolved when a large volume of oxygen is blown into the bath during melting and refining, and if the gas is completely burned over the bath, the heat evolved will be substantially greater than is needed for the process.

It would be rational to add iron ore to the bath as a coolant at that time, but this cannot be done because of the danger of slag and metal splashing on the stage. The problem of using the huge volume of heated carbon monoxide evolved from the bath has been successfully solved by developing a new way of making steel in a twin-bath furnace.

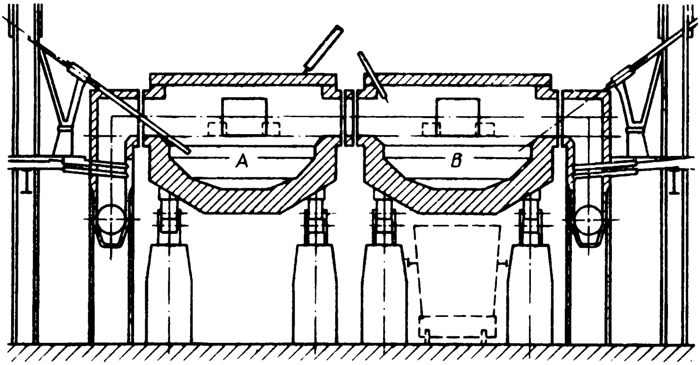


Fig. 110. Schematic diagram of a twin-bath open-hearth furnace

Let two baths, *A* and *B*, with a common roof be connected by a passage through which gases can move (Fig. 110). Each of the baths has a taphole, a higher hole in the rear wall for skimming off the slag during melting, and charging doors, one of which has a lower sill for letting out the overflowing slag.

The process of making steel in a twin-bath furnace is as follows. While the metal in bath *A* is being blown with oxygen, bath *B* is charged with scrap and loose materials, which are heated up with the flame from bath *A* , thus regenerating part of its heat. The fuel for bath *B* is mainly the carbon monoxide in the fumes passing through the passage from bath *A*, motion of the gases being provided by the draught of the stack and by an ejector nozzle mounted in the roof above bath *B*. The carbon monoxide coming from bath *A* is burned with the oxygen jet. It should be noted that no fuel is supplied, as a rule, when *bath A* is being blown with oxygen; if, however, fuel is supplied, it is burned in the flow of oxygen, so that the fumes passing to bath *B* have quite a high concentration of hot CO.

In addition, there are oxygen lances in the roof above bath *B*, and also gas-oxygen burners to supply more fuel to heat up scrap and fluxes when needed.

As the metal is tapped from bath *A* , the direction of fumes is reversed from bath *B* to bath *A*, after which pig iron is charged into bath *B* over the preheated scrap, ore, and fluxes. Then oxygen blowing is started in bath *B*, while bath *A* is being charged with scrap, ore and fluxes, i.e., a new cycle of operation is started. Bath *A* has oxygen lances, gas-oxygen burners, and an ejector nozzle installed in its roof, as in bath *B*.

With specified amounts and compositions of pig iron and scrap in the charge, the intensity of oxygen blowing of the baths must be so adjusted that the time taken for fettling and charging, heating and pouring iron in one bath can be equal to the length of melting and refining periods in the other bath. This ensures equality of the thermal balance in each bath. When chemically cold (inactive) pig iron is used, or when the proportion of iron in the charge is small, it may be necessary to correct the thermal conditions in the furnace by supplying additional fuel through the gas-oxygen burners.

At the Cherepovetsky works in the USSR, there is a twin-bath furnace of a capacity of 300 tons in each of the baths, operating on a charge composed of 60 per cent chemically cold molten pig iron and 40 per cent scrap. The design duration of the whole cycle is $3^1/_2$ hours, with tappings every 105 minutes. The furnace has no regenerators and therefore is cheaper in construction and maintenance. Each bath has three oxygen lances, seven gas-oxygen burners, an ejector nozzle in the roof, and two supplementary gas-oxygen burners at each end of the furnace. Even in the running-in period, the productivity was as high as 119.5 t/h (and up to 146.4 t/h in the best heats), with a fuel consumption of only 29 kg per ton steel, but the unit oxygen usage was more than 60 m^3. The annual output by the furnace is more than 1,200,000 tons of steel.

At some iron and steel works in the USSR (Magnitogorsky, Krivorozhstal, Zaporozhstal, etc.), a number of open-hearth furnaces have been reconstructed into twin-bath units and are operated with a charge of about 65 per cent liquid iron and 35 per cent scrap. Their productivity is rather high and the consumption of fuel and refractories low.

The slags of a twin-bath furnace have a high concentration of oxides of di- and tri-valent iron during the whole heat. The rate of carbon oxidation reaches 0.015-0.024 per cent per minute with a carbon content in the bath below 0.4 per cent, and increases to 0.019-0.027 per cent C/min at higher carbon concentrations.

The dust content in combustion products reaches 15-20 g/m^3. Experiments in blowing the bath with a gas-oxygen mixture (32 m^3 of natural gas plus 45 m^3 of oxygen per ton steel) resulted in less dust formed.

The high losses of iron with overflowing slags, beads, and dust, and low ore content of the charge (sometimes no iron ore at all) in these furnaces result in a low yield of metal (88.3 per cent). This is an indication that further improvements are needed in the twin-bath process.

The advantages of twin-bath furnaces over conventional ones are that they are simpler in design, require less capital outlay, use less refractories and fuel, have higher productivity, and produce metal regularly in small portions (300 tons), which facilitates efficient operation of the stripper yard and soaking-pit department. Twin-bath furnaces are also operated in the USA, Canada, the Republic of South Africa, Czechoslovakia, and Poland.

CONVERSION OF HIGH-PHOSPHORUS PIG IRON

A number of processes have been developed for converting high-phosphorus pig irons in open-hearth furnaces, tilting-type furnaces being usually employed for the purpose.

The Talbot process. Steel is made in tilting furnaces of a capacity of 150-350 tons. After the metal has reached the specified composition, the furnace is rapidly tilted to the pit side to tap the metal partially (without letting out the slag), deoxidation and carbonization of the tapped metal being carried out in the launder or ladle. In the earlier practice of the process, up to 40 per cent of the metal used to be tapped, but in recent practice 70 to 90 per cent of the metallic bath is tapped. After tapping, the banks are fettled and the slag left in the furnace is activated by adding calcined lime and iron ore, after which scrap is charged.

After the slag has been formed, pig iron is carefully poured in in an amount required to bring the charge to the specified mass. The violent reactions of oxidation of carbon, phosphorus and other impurities result in the slag being enriched with phosphorus oxides and impoverished in iron. The high-phosphorus slag is then run off by tilting the furnace toward the stage, after which a new slag is formed by adding lime and iron ore, and the oxidation of impurities is carried out in the usual way to obtain low-carbon steel. The metal is then partially tapped and a new cycle started.

The Azovstal process. A 400-ton tilting furnace is charged with 25 per cent scrap and 75 per cent liquid iron of the following composition: 0.45-0.55 per cent Si, 1.8-2.0 per cent Mn, 0.065 per cent S, and 1.5-1.6 per cent P. The furnace is fired with natural gas to make rail steel or rimming steel.

The tap-to-tap time is shortened by supplying oxygen-enriched air (up to 29 per cent O_2) during the periods of charging, heating, and iron pouring. The high-oxidizing flame ensures rapid formation of high-ferruginous basic (up to 38 per cent CaO) dephosphorizing slags.

Rail steels of a relatively high carbon content can be produced from high-phosphorus pig iron only if dephosphorization during the melting period is carried out to a maximum. The required conditions are formed by introducing oxygen directly into the bath.

With the combined method of using oxygen (Table 44), the process is speeded up and less fuel and oxygen are consumed without impairing the quality of the phosphate slag.

In the bath blown with oxygen, the rate of carbon oxidation increases up to 0.7-0.9 per cent per hour, and also does

Table 44

Efficiency of Combined Use of Oxygen

Characteristics	Heats with oxygen-enriched air	Heats with oxygen lancing during melting, m^3			
		up to 900	900-1800	1800-2700	2700-3600
Number of heats	18	12	18	7	4
Melting plus refining, h-min . .	9-20	8-43	8-00	7-13	6-29
Oxygen consumption to enrich air, m^3 per heat . .	9840	7750	6460	6370	4840
Oxygen for direct oxidation in the bath during melting, m^3	—	720	1280	2160	3020
Oxygen for direct oxidation during boiling, m^3/h . .	—	800	855	1080	1405
Unit oxygen consumption, m^3/t	28.3	26.6	24.7	27.7	26.1
Unit fuel consumption, kg/t . . .	163.2	158.0	155.7	152.2	140.5
Mass of charge, tons	352.4	350.6	351.8	352.6	354.6
Charged, tons:					
pig iron . . .	262.5	270.6	271.3	268.0	264.0
scrap	89.9	80.0	80.5	84.6	90.6
iron ore . . .	30.8	33.8	33.4	30.3	31.3
limestone . .	25.5	23.2	22.4	22.3	21.5
Oxidation rate during melting, %/h:					
carbon	0.30	0.39	0.42	0.51	0.58
phosphorus . .	0.227	0.258	0.313	0.370	0.394

Table 44 (continued)

Characteristics	Heats with oxygen-enriched air	Heats with oxygen lancing during melting, m³			
		up to 900	900-1800	1800-2700	2700-3600
Oxidation rate during refining, %/h:					
carbon	0.190	0.172	0.200	0.204	0.204
phosphorus	0.021	0.026	0.021	0.022	0.018
Slag analysis on meltdown, %:					
CaO	39.0	37.5	40.0	34.1	36.0
SiO_2	13.7	13.1	13.5	13.8	13.7
FeO	7.65	11.35	9.12	11.24	15.5
P_2O_5	17.45	17.30	17.46	17.55	16.61

the rate of oxidation of phosphorus. This is linked with the fact that the bubbling caused by oxidation of carbon results in intense intermixing of the metal and slag which accelerates the exchange reactions between them.

The periods of melting and refining are reduced depending on the amount of oxygen introduced into the bath (up to 32.0 per cent) compared with their duration when the operation is carried out with oxygen being supplied only to the flame.

The process for making rail steel is performed at the Azovstal works as follows. Upon tapping a furnace, about 20 tons of steel and the whole amount of slag are left in it, the latter containing 43-47 per cent CaO, 8-13 per cent FeO, 5-7 per cent P_2O_5, and 7-9 per cent SiO_2, after which limestone, iron ore, and steel scrap are charged in succession. After heating these materials for 40-50 minutes, the whole amount of pig iron is poured in.

About an hour later, the phosphate slag (the first two slag ladles) is skimmed off, its composition being 13-14 per cent P_2O_5, 10-12 per cent FeO, 28-32 per cent CaO, 14-18 per cent MnO, and 18-20 per cent SiO_2. The slag in two subsequent slag ladles (skimmed off 2.0-2.5 h after pouring in pig iron) contains 15-18 per cent P_2O_5, 34-38 per cent CaO, 8-10 per cent FeO, 10-12 per cent MnO, 14-17 per cent SiO_2.

After the phosphate slags have been skimmed off, a new slag is formed by adding lime, mill scale, and bauxite, and under its cover the refining and pure boiling of the bath are carried out. During the second half of the refining period, the slag so formed contains 46-48 per cent CaO, 6-9 per cent SiO_2 and 6-7 per cent P_2O_5 and has a basicity of 3.5-3.8. Excess slag is skimmed off to activate boiling, which lasts 30-40 minutes.

When the bath contains 0.62-0.65 per cent C, all the specified high-carbon manganese is added and the furnace is then tapped, 45-% ferro-silicon and aluminium being added into the ladle. A heat-insulating mixture is spread over the metal surface in the first ladle. While filling the second ladle, ferro-silicon is to be added as soon as possible. The furnace slag that occasionally passes into the ladle is made thick by adding dolomite and lime to prevent reduction of phosphorus from it. After tapping, about 20 tons of steel and the whole amount of the final slag are left in the furnace, and the melt cycle is then repeated.

The Ajax process. A new process, known as the Ajax process, has been developed at the Appleby Frodingham Works in Great Britain for making steel in six tilting open-hearth furnaces of a capacity of 300 tons each. The charge consists of 100 per cent high-phosphorus liquid iron pretreated in an active mixer. The furnaces are fired with coke-oven gas and fuel oil. Oxygen consumption to intensify combustion does not exceed 5 m^3 per ton steel. Three nozzle lances for the blowing of the bath are mounted in the roof above the ports at an angle of 27-34 degrees to the bath surface. Oxygen is blown at a rate of about 25 m^3 per ton steel. The yield of liquid steel in the process is approximately 92 per cent and the heat load, $0.227 \cdot 10^6$ kcal per ton steel (Fig. 111).

The furnaces used in the process have been improved somewhat in their design, namely, two slag chambers and two cylindrical regenerators encased in metal are installed at each end of the furnace, the regenerators being operated alternatively. Owing to the provision of movable uptakes,

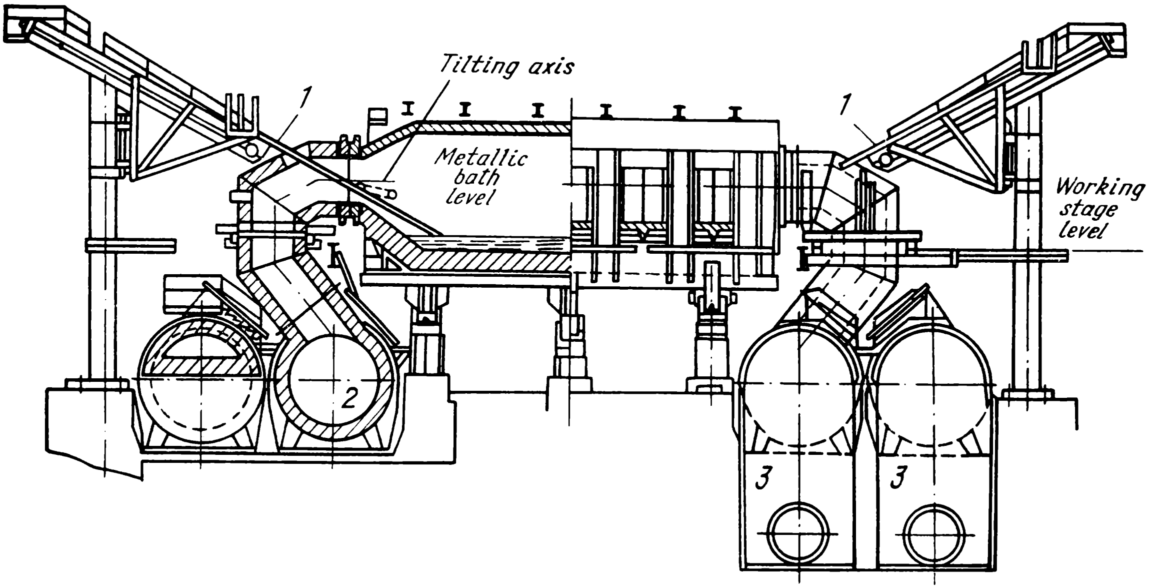


Fig. 111. Diagram of an Ajax furnace
1—oxygen lances; *2*—slag chamber; *3*—regenerators

the switch-over from one regenerator and slag chamber to the other pair can be made in a few hours without stopping the furnace, and is done every four weeks of furnace operation. These units can easily be replaced by means of an overhead crane and moved for repair to a special place in the shop.

Higher productivity at lower operating cost is obtained with furnaces of this type than with the standard type. After tapping, roughly 20 tons of metal and the whole amount of the final slag are left in the furnace. Fuel supply is interrupted for the period of blowing of the bath with oxygen (which is done at a rate of 2300 m^3/h). The furnaces are used for making soft steel to be rolled into sheets for deep drawing.

TECHNICO-ECONOMICAL INDICES OF THE BASIC OPEN-HEARTH PROCESS

The principal indices of steelmaking in open-hearth furnaces are the furnace productivity and the cost of a ton of the steel produced. The efficiency of operation of open-hearth furnaces is evaluated in terms of their hourly or annual productivity. The index of daily steel production per square metre of the hearth area is sometimes used. But since the area of the hearth is not constant and is rather conditional, it is better to employ the indices of daily or annual furnace productivity in sound ingots.

Cold standstills of a furnace are the time spent on all the repairs made after complete cooling of the reaction chamber plus the time required for drying and heating the furnace after the repairs. Hot standstills are all the intermissions in the furnace operation between heats and also furnace repairs with the charge (melt) left in the bath, which do not entail full cooling of the furnace or temporary stoppage of the process of steelmaking.

The nominal time of furnace operation is the time during which the furnace has been in hot state; it is equal to the calendar time of its operation during a given period less the time spent for cold repairs. The nominal time is the productional time and in turn can be divided into the actual time of furnace operation and the time of hot standstills. Thus, the actual time of furnace operation is the nominal time minus the time spent for hot standstills.

At the advanced steelmaking works in the USSR the time of hot and cold repairs is 6 to 7 per cent, i.e., a furnace is in operation 340-343 days a year and 22-25 days is under repairs.

Let us calculate approximately the productivity of a 500-ton open-hearth furnace operating by the scrap-and-ore process with oxygen being used only for bath blowing. The furnace is run for rimming steel with four tappings being made each day. The yield of sound ingots in each melt is 92 per cent of the mass of the metallic charge on the average. The hourly productivity is 500 × 0.92 : 6 = 76.66 tons; the annual productivity will then be 500 × 0.92 × 4 × × 340 = 625,600 tons of sound ingots.

When making quality and alloy steels, the time of a heat increases somewhat and the furnace productivity reduces. In planning the production, this is taken into account by introducing a factor for each grade of steel to be made, the value of this factor varying from 1.0 to 1.25.

Taking the area of the hearth of the 500-ton furnace to be 105 m^2 (counting from the level of door sills), the yield of steel will be 76.66 × 24 : 105 = 17.5 $t/m^2 \cdot$day.

The annual productivity is the principal index of furnace operation. If the furnace is run with varying intensity and with frequent standstills during a year, its annual index will be low.

At present, the expected annual productivity of furnaces of various capacity is calculated taking into consideration the intensification means to be employed. These indices with due regard for planned standstills and repairs, and also the consumption of fuel and refractories are given in Table 45.

As can be seen from the table, the technico-economical indices of furnace operation are improved with an increase of furnace capacity; this also relates to the cost of steel and labour productivity.

An index of importance is the consumption of metallic charge to make one ton of final steel. At all works in the USSR, metallic charge is used according to a planned norm. At advanced works, such as Magnitogorsky and Kuznetsky

Table 45

Planned Operational Indices of Open-hearth Shops

Index	Furnace charge (pig iron and scrap), t									
	50	100	130	200	250	300	400	500	600	900
Annual productivity in the pig-and-scrap process without oxygen, tons of sound ingots	75 000	110 000	130 000	170 000	190 000	220 000	—	—	—	—
Annual productivity in the scrap-and-ore process with moderate oxygen blowing, tons of sound ingots	—	—	—	310 000	340 000	370 000	430 000	500 000	570 000	800 000
Ditto, with high intensity of blowing	—	—	—	540 000	570 000	600 000	670 000	740 000	810 000	1 000 000
Total standstills (hot and cold), % of calendar time	6	6	6	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Hour productivity in the pig-and-scrap process without oxygen, tons	9.1	13.4	15.8	20.6	23.0	26.6	—	—	—	—
Hour productivity in the scrap-and-ore process with moderate oxygen blowing	—	—	—	38.5	41.0	45.0	52.0	60.5	69.0	96.5
Ditto, with high intensity of blowing	—	—	—	65.0	69.0	72.5	81.0	89.5	98.0	121.0

Table 46

Structure of Cost of 1 ton of Ingots of Open-hearth Carbon Steel, Percentages

Cost component	Process	
	scrap-and-ore	pig-and-scrap
Metallic charge materials (pig iron, scrap, ferro-alloys)	82-72	77-64
Auxiliary materials (iron ore, limestone, lime, bauxite, etc.)	4-5	3-1
Cost of conversion	13-23	19-34
including:		
process fuel (fuel oil, gas, etc).	3-4	6-8
cost of power (electric energy, water, steam, compressed air, oxygen)	1.2-2.3	2.2-3.2
wages	0.8-2.5	2.4-4.0
depreciation	1.2-1.5	0.9-3.0
current repairs, including the cost of refractories, maintenance of capital means of production, wear of replaceable equipment (moulds, bottom plates, etc.)	4.4-8.1	5.2-9.0
transport facilities	0.7-1.4	0.6-1.8
other expenses in the shop	0.7-1.8	0.8-1.8
Works expenses	1.0-1.4	0.9-3.2

integrated works, this index is kept at a very good level owing to proper organization of production, well worked out steelmaking technology, and a minimum loss of metal as rejects.

The cost of steel depends on a number of factors, including the structure of the plant (with or without the complete metallurgical cycle), furnace capacity, equipment of units, composition of charge, kind of fuel, and skill of operators and engineering personnel. For instance, the cost of steel at modern integrated works is noticeably lower than at older works (the cost of common killed carbon steel varies between 68 and 78 roubles per ton).

The structure of the cost of open-hearth steel is given in Table 46, from which it follows that its main component is the cost of charge materials. The consumption of individual components of the charge depends on the type of process, method of teeming (direct, uphill or in continuous casting plants), the amount of short-run and rejected ingots, ladle skull, etc. With a properly organized production at advanced works the percentage of rejected metal does not exceed 0.4-0.6. The weight of metallic charge per ton of sound ingots is 1150-1100 kg in the scrap-and-ore process and 1100-1170 kg in the pig-and-scrap process. The yield of sound ingots is the inverse of the consumption of metallic charge. For instance, if the consumption of metallic charge is 1086 kg, the yield of sound ingots will be $1 : 1.086 = 0.92$ or 92 per cent.

The cost of charge materials can be reduced by proper sorting of carbon and alloy steel scrap in the shop. The use of alloy steel scrap is less expensive than the addition of ferro-alloys and alloying elements in melt finishing.

One of the main components in the structure of the cost of steel is the cost of conversion. Maintaining of the units in working state, proper production organization to prevent bottlenecks in the shop, application of the most advanced equipment, improvement of the skill of steelmakers—all these factors are decisive in reducing the tap-to-tap time, increasing the life of furnace elements, shortening standstills, and saving fuel. Optimum thermal conditions and automatic control of the thermal process can give a substantial fuel economy. At advanced plants the consumption of standard fuel is 110-130 kg/t steel in operation without oxygen. All these methods of improving the production and the high engineering culture of the personnel give a reduction in the cost of conversion. With old plants and poor technical equipment the cost of conversion is substantially higher than at works having a high level of mechanization of production.

The cost of refractories plays an important part in decreasing this index. Guniting of the walls and roof of furnaces is an effective method for increasing the life of lining, though it is not widely employed so far. The life of the roof can be prolonged by periodically blowing it with air; this also can save refractories.

Production of steam in waste-heat boilers and of commercial phosphate slags (in cases of conversion of high-phosphorus pig iron) is a factor of importance for decreasing the cost of conversion, since the cost of steam and slag produced can then be subtracted from the cost of steel.

At works operating by the incomplete metallurgical cycle the cost of steel is higher on account of a lower capacity of furnaces, a small scale of production, and a high percentage of some shop's and works' expenses.

The most important factor for decreasing the cost of steel is an increase of labour productivity, i.e., the amount of steel made per year per worker. All workers and engineers of the shop are responsible for this index. They should take care of mechanization of labour-consuming operations, automation of thermal and process conditions of heats, and implementation of new engineering achievements into the production. Steelmakers and foremen should be periodically trained in order to improve their skill and should be involved into inventive and rationalization activities. In advanced open-hearth shops operating by the scrap-and-ore process the productivity is such that more than 4000 ton steel is produced annually per worker; accordingly, the cost of steel produced is very low.

Chapter Fifteen

THE ACID OPEN-HEARTH PROCESS

Starting materials for the acid process. For economic considerations, the acid open-hearth process is only suitable for making high-quality steels, the cost of which is not too dependent on the price of costly starting materials which must be very low in phosphorus and sulphur. These impurities cannot be refined in acid open-hearth furnaces, and therefore the starting materials and fuel to be used in the process must meet more rigorous requirements as regards their contents.

High-grade pig iron containing not more than 0.015-0.020 per cent P and 0.01-0.025 per cent S is most suitable for the acid process. It is produced in charcoal-fired blast furnaces or sometimes in furnaces fired with pure coke. The liquid fuel (fuel oil) for firing acid furnaces must have not more that 0.3-0.5 per cent S. In the practice of acid open-hearth steelmaking, pig iron is sometimes replaced with carburizers (petroleum coke or graphite), the silicon and manganese required for the melt being then introduced into the charge with return acid slag and manganese ore.

The choice of scrap for the acid process also presents certain difficulties in keeping the phosphorus and sulphur contents as low as possible. The problem is often solved by using a duplex process: basic open hearth—acid open hearth, the former producing a semiproduct refined of phosphorus and sulphur in the form of ingots or billets. If both furnaces are located in the same shop, the liquid metal produced in the basic furnace is transferred directly into the acid one.

The metallic charge is usually made up so as to have a carbon content on meltdown 0.6-0.8 per cent higher than the specification. In solid-charge operation, the metal on meltdown often proves to be not fully covered with slag, so that sand or return slag must be immediately introduced into the furnace (in an amount of 3.5-4.5 per cent of the metallic charge) to prevent excessive oxidation of the melt. When an acid furnace is run with using liquid semiproduct from a basic furnace, return slag is added before pouring the semiproduct into the acid furnace, the metal being poured through the stopper of the ladle via a chute through the rear wall of the furnace in order to prevent passage of the slag from the ladle.

Two variants of the acid process are employed: (1) a silicon-reducing or passive and (2) an active process with partial reduction of silicon.

The passive (silicon-reducing) process. The passive process makes it possible to reduce silicon to its specified content in the final steel.

When the manganese content of the charge is sufficiently high, manganese will be reduced at the same time as silicon; the version is therefore sometimes called the silicon-manganese-reducing process.

Reduction of silicon requires a high temperature of the process and a weakly acid slag saturated with SiO_2. The influence of slags on silicon reduction is linked with their fluidity, as well as with their chemical composition. With a SiO_2 concentration of 50 to 54 per cent the slag is free-running, while at higher concentrations (up to 55-62 per cent) it becomes thick and clearly heterogeneous. The passage of oxygen through such slags from the gaseous phase is greatly slowed down, which favours the reduction of silicon by the carbon, manganese, and iron of the bath.

With any version of the acid process, the slags tend to become saturated with SiO_2 (50-60 per cent) by the end of the process. Addition of CaO to the slag increases the solubility of SiO_2, decreases the FeO content of the slag, and slightly decreases the rate of refining of the bath.

Variations in the composition of a high-silica slag during the melt are given in Table 47. As soon as the maximum reduction of silicon is attained and carbon oxidation is finished, the FeO content begins to rise in the upper layers of the slag, without having an influence on the metallic bath.

Table 47

Composition of Steel and Slag in the Silicon-reducing Process

Sample	Time, min	Temperature, °C	Composition, per cent					
			slag			steel		
			SiO_2	FeO	MnO	C	Mn	Si
1	0	1570	50.2	8.1	36.2	0.86	0.43	0.10
2	60	1590	53.3	7.8	33.7	0.67	0.46	0.18
3	120	1610	56.7	8.1	31.4	0.54	0.50	0.27
4	150	1620	57.2	9.1	30.7	0.46	0.50	0.32
5	180	1630	57.2	9.3	30.0	0.41	0.49	0.35
6	210	1630	55.8	11.5	28.2	0.38	0.50	0.37
7	240	1620	55.5	11.9	27.8	0.37	0.50	0.37
8	300	1620	53.9	14.7	25.5	0.36	0.48	0.37

Silicon can only be reduced when the slag has a weak oxidizing power; for this, it must contain not much free FeO and MnO and, on the contrary, have a sufficiently high amount of free SiO_2. The oxidizing power of the slag is easy to control in practice by adding sand or fireclay. The hearth and banks of the furnace, and also the particles of SiO_2 detached from them and suspended in the molten bath, are the main elements in the reaction of reduction of silicon, while only part of the slag is actively involved in the reaction, namely the layer which is in immediate contact with the liquid metal.

The reduced silicon dissolved in the bath is partially reoxidized by the oxygen from the slag, so that its content in the metallic bath is always determined by the difference between the quantity reduced and that reoxidized.

Thus, silicon moves from the hearth to the slag. The working layer of the hearth thus loses silicon and in practice must be renewed by fettling it thoroughly before each heat.

As follows from Table 47, an increase in the SiO_2 content of the slag causes an increase of the silicon concentration in the metal. The process of reduction of silicon thus can be easily controlled by varying the oxidizing power of the slag, for instance, by spreading iron ore, mill scale or lime over it.

Stronger reduction of silicon is observed at a high temperature of the bath when the activity of carbon reaches its maximum and the slag becomes low in iron and manganese:

$$(SiO_2) + 2[C] \rightarrow [Si] + 2\{CO\} - Q$$

$$(SiO_2) + 2[Fe] \rightarrow [Si] + 2(FeO) - Q$$

$$(SiO_2) + 2[Mn] \rightarrow [Si] + 2(MnO) - Q$$

The reactions of reduction of iron and manganese from the slag by carbon

$$(FeO) + [C] \rightarrow [Fe] + \{CO\} - Q$$

$$(MnO) + [C] \rightarrow [Mn] + \{CO\} - Q$$

which occur simultaneously with the former reactions, indirectly promote silicon reduction by diminishing the oxidizing power of the slag. Iron can act as a reducer of silicon only at a very low concentration of oxygen in the metal. Manganese, too, can act as a silicon reducer under certain conditions, for instance, when high-manganese pig iron is used in the charge.

It can be concluded from the foregoing that silicon reduction occurs through the interaction of the carbon, manganese, and iron in the bath with the SiO_2 of the hearth, this interaction tending to equilibrium during the heat. A similar conclusion about the interaction of the metal and slag, however, would be unfounded because of the continuous oxidation of the slag and its nonhomogeneous composition and physical state resulting from its low fluidity at SiO_2 concentrations above the saturation point.

The interaction between the slag and the gaseous oxidizing atmosphere tends to equilibrium, so that the slag becomes high in iron oxides. The rate of pick-up of iron oxides by the slag during the period of silicon reduction exceeds the rate of passage of oxygen from slag to metal. For that reason the two processes, i.e., the growth of the silicon concentration in the metal and the growth of the FeO concentration in the slag, occur simultaneously despite the seeming contradiction.

A typical example of the silicon-reducing process with solid charge is provided by the graph in Fig. 112 relating to a melt in which silicon was reduced to 0.24 per cent. The heat of an open-hearth furnace with a 16-ton charge took 12 hours, of which 5 hours 20 minutes were needed for boiling and adding of ferro-alloys. The long period of "stabilization" of the bath in the typical silicon-reducing process substantially lowers the productivity of the furnace and raises the cost of the final steel. The rate of burning off of carbon during the stabilization period is extremely low (0.05-0.10 per cent C per hour).

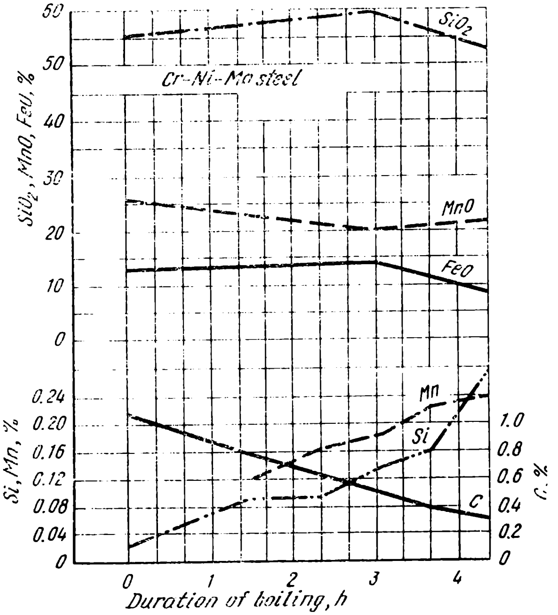


Fig. 112. Graph of the silicon-reducing process (after V.I. Tyzhnov)

Figure 113 shows the graph of melting of a 50-ton charge consisting of pig iron and liquid semiproduct by the silicon-reducing version (duplex process). Silicon was reduced to 0.33 per cent, which entailed no enrichment of the steel in nitrogen, because silicate slags are impermeable to this gas. An essential advantage of this process is the possibility of finishing the heat without adding deoxidants, or only a very small quantity, i.e., without contaminating the steel with non-metallic inclusions. This is why acid steels are less anisotropic in their properties, especially in the impact strength, than basic steels.

Economically speaking, the lower wastage of metal (through flakes, woody fracture, and other ingot defects caused by the presence of hydrogen) completely justifies the longer duration of the heat compared with that of the ordinary version of the process.

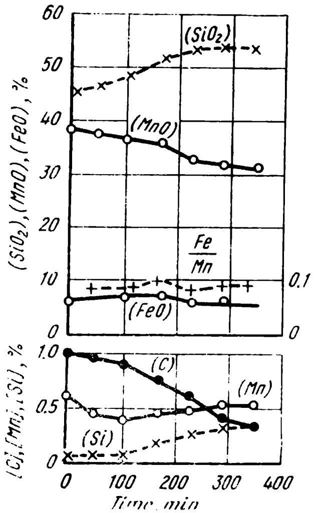


Fig. 113. Graph of the silicon-reducing process using molten semiproduct (after P. Gerasimenko)

THE ACTIVE ACID PROCESS WITH PARTIAL REDUCTION OF SILICON

In the active acid process it is permissible to reduce silicon to a level of 0.10-0.12 per cent. The reaction of reduction of silicon is slowed down by spreading small amounts of iron ore or mill scale over the slag, thereby increasing the oxidizing power of the slag and simultaneously decreasing the bath temperature. This gives an immediate desired effect and not only prevents further increase in the silicon content of the metal, but also can remove the silicon already reduced into the slag. Lime can act in combining some of the SiO_2 into stable silicate compounds, thus decreasing the concentration of free SiO_2 in the slag. Besides, it makes the slag more fluid and therefore more capable of transferring oxygen from the furnace atmosphere to the metal:

$$(FeO \cdot SiO_2) + (CaO) = (CaO \cdot SiO_2) + (FeO)$$

The reverse side of the action of CaO, however, must not be disregarded, i.e., its ability to increase the solubility of SiO_2 in slag, since iron and manganese bisilicates $FeO \cdot SiO_2$ and $MnO \cdot SiO_2$ contain 45.5 per cent SiO_2 each, while calcium bisilicate $CaO \cdot SiO_2$ contains 51.75 per cent SiO_2.

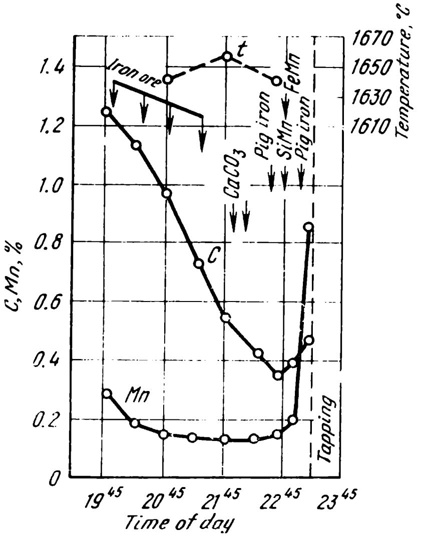


Fig. 114. Graph of a melt by the active acid process (after M. Yakhnenko)

For that reason, the concentration of free SiO_2 in the slag diminishes and the reaction

$$SiO_2 + 2Fe \rightleftarrows 2FeO + Si$$

is reversed to the left*.

In practice, the content of CaO in slag usually does not exceed 5 per cent. When lime is added to slag, iron and manganese oxides in silicates are displaced by the reactions:

---

* According to the reports of some researchers, silicon oxide SiO is present in the solution of molten iron. The silicon content of a molten bath determined by chemical analysis is represented by the sum of $Si + SiO + SiO_2$, the solubility of SiO_2 in liquid steel not exceeding 0.003 per cent, while that of SiO is 100-150 times higher. The dominant member of the sum is therefore SiO.

$$(FeO)_2 \cdot SiO_2 + 2CaO = (CaO)_2SiO_2 + 2FeO$$

$$(MnO)_2 \cdot SiO_2 + 2CaO = (CaO)_2SiO_2 + 2MnO$$

The oxidizing power of the slag is thus temporarily increased, but through the subsequent reactions with carbon the slag becomes low in FeO and MnO. The slags of the active acid process, therefore, differ substantially from those of the silicon-reducing process in having lower contents of FeO and MnO.

The active acid process with the use of liquid semiproduct was employed at the Novo-Kramatorsky works. The reduction of silicon was limited to a level of 0.1 per cent, which was ensured by adding limestone several times, the last lot not later than a half-hour before the preliminary deoxidation of the bath with pig iron.

The approximate composition of the final slags of two melts before adding finishing products was (percentages):

SiO_2	CaO	MnO	FeO	Al_2O_3
55.4	4.2	18.2	14.31	6.2
57.4	3.9	19.0	14.10	2.6

The course of the process is shown in Fig. 114. The steel produced had the following analysis: 0.47 per cent C, 0.85 per cent Mn, 0.019 per cent S, 0.034 per cent P, and 0.33 per cent Si.

The course of the active acid process with solid charge (from British practice) is shown in Fig. 115. The slag at the initial stage of the heat was more oxidizing than at the end of the heat. Its SiO_2 content was in excess of that required for the formation of silicates $MnO \cdot SiO_2$, $(CaO)_2SiO_2$, $CaO \cdot SiO_2$, and $(FeO)_2 \cdot SiO_2$ or $FeO \cdot SiO_2$.

By periodic additions of iron ore and limestone to the slag in the course of the heat, the oxidizing ability of the slag was kept at such a level as to prevent excessive reduction of silicon.

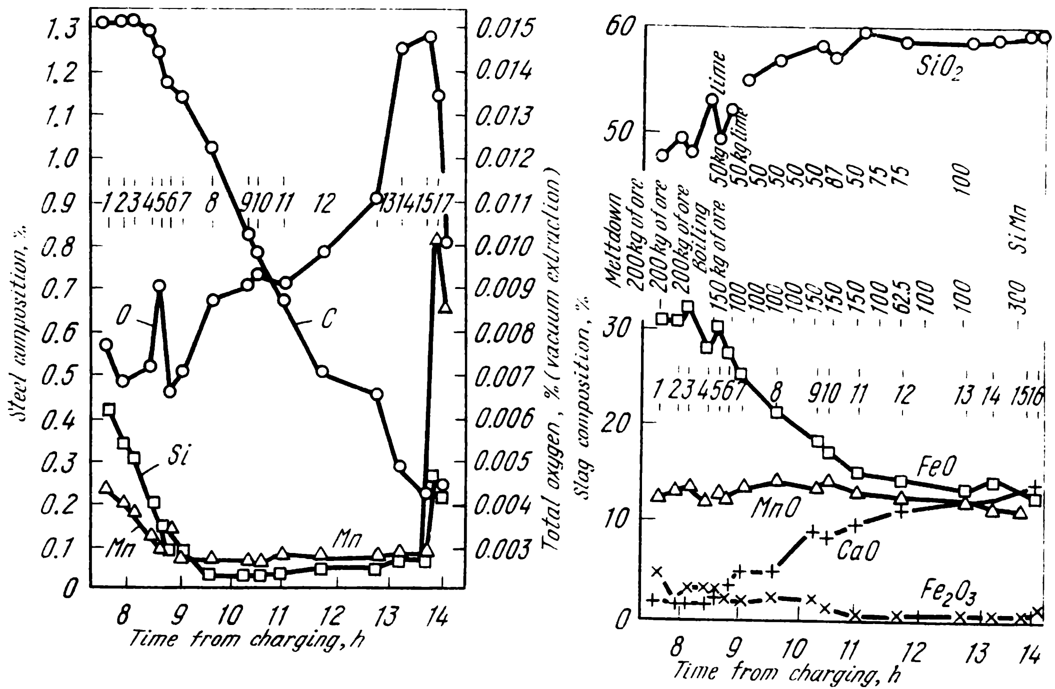


Fig. 115. Graph of a melt by the active process (British practice)

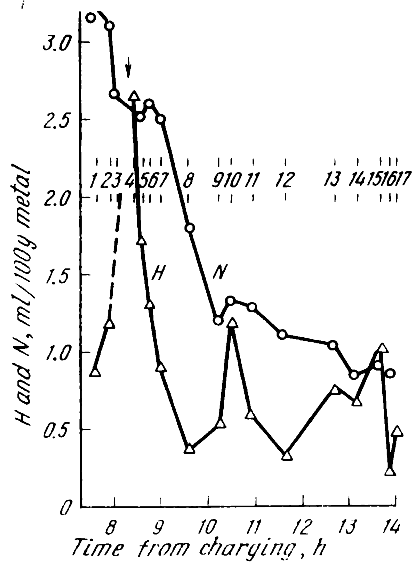


Fig. 116. Variations of hydrogen and nitrogen content in a melt by the active acid process

A long period of quite intensive boiling favoured renfiing of the metal from the dissolved hydrogen and nitrogen (Fig. 116).

COMPARISON OF THE PASSIVE AND ACTIVE PROCESSES

The high quality of steel made in an acid open-hearth furnace is due to the fact that the liquid metallic bath free of sulphur and phosphorus is enclosed into a 'shell' of silicon oxides (in the hearth, banks, and slag cover). The oxygen dissolved in the metal is extracted by that shell by the general reactions $[FeO]_n + (SiO_2)_m = (FeO)_n(SiO_2)_m$. This has been confirmed by the analyses of samples of the lining of hearth; the surface layers in contact with metal are rich in iron oxides (and low in SiO_2). In deeper layers of the lining the content of iron oxides decreases and that of SiO_2 increases. This is why the working layer of the hearth must be fettled after each heat.

Therefore, acid steels contain less dissolved oxygen than basic grades.

Thick slags, especially in the passive process, where they have only a weak oxidizing power, prevent the passage of gases from the furnace atmosphere into the metal. And finally, since deoxidation is dispensed with, the metal produced is very low in nonmetallics and gases. In the active process, the amount of deoxidants used in the heat is also not high since the bath oxidizes insignificantly compared with the basic process.

On the other hand, some phenomena occurring in the acid open-hearth process have not yet been explained properly. For instance, the metal in a sample taken when the silicon in the bath has been reduced to 0.12-0.15 per cent usually grows in volume and contains many gas bubbles. The opponents of the passive process used this fact more than once to claim that this process indeed leads to gas saturation of the metal. Ianeske and Wood even attempted to explain the bubbling of metal samples by the presence of excess oxygen in the solution, depicting the process causing this defect by the reaction

$$SiO_2 + Fe \rightarrow FeSi + 2[O]$$

The rivalry of the passive and active processes favoured the development of both.

Table 48

Advantages (+) and Drawbacks (−) of the Active and Passive Processes

Version	Tap-to-tap time	Consumption of ferro-alloys	Consumption of iron ore and limestone	Steel yield	Slag yield	Labour cost	Wastage
Silicon-reducing (passive) process . .	−	+	+	−	+	+	+
Active process with partial reduction of silicon . .	+	−	−	+	−	−	

The two processes may be compared as shown in Table 48; a detailed economic analysis is required to decide between them in any particular case.

The acid open-hearth process is now employed for making steel for crankshafts, large turbine rotors, heavy-duty bearings, artillery guns, etc. Steel is cast into large ingots (100-300 t) in which the chemical heterogeneity is insignificant owing to low concentrations of sulphur and phosphorus.

THE DUPLEX PROCESS: BASIC PLUS ACID OPEN-HEARTH FURNACES

The metal in an acid open-hearth furnace cannot be refined from phosphorus and sulphur. Because of this, combined operation of basic and acid furnaces for making quality steels has found wide application in many countries. The term 'duplex process' is sometimes applied to the operation of an acid open-hearth furnace with the use of ingots of a semiproduct specially made in a basic furnace. These ingots are most often cast from rimming steels low in harmful impurities, but sometimes from alloyed steels of a high carbon content.

The duplex process proper, i.e, basic open-hearth plus acid open-hearth furnace, may be carried out by either of the two following versions.

(1) the charge for the acid furnace is made up of liquid semiproduct from the basic furnace and high-quality pig iron sufficient for carbonization of the bath; or

(2) a liquid semiproduct containing 0.8-1.0 per cent C, 0.5-0.6 per cent Mn, up to 0.02 per cent S, and up to 0.02 per cent P is made in the basic furnace; its carbon content ensures the necessary boiling of the bath in the acid furnace; high-quality pig iron is then not required.

Figures 117 and 118 give examples of the second version. As will be seen from the graphs, dephosphorization and desulphurization are completed in the basic furnace and the metal, after being deoxidized by ferro-manganese and containing 1.32 per cent C, is poured into the acid furnace, which is first charged with the return slag from the previous melts.

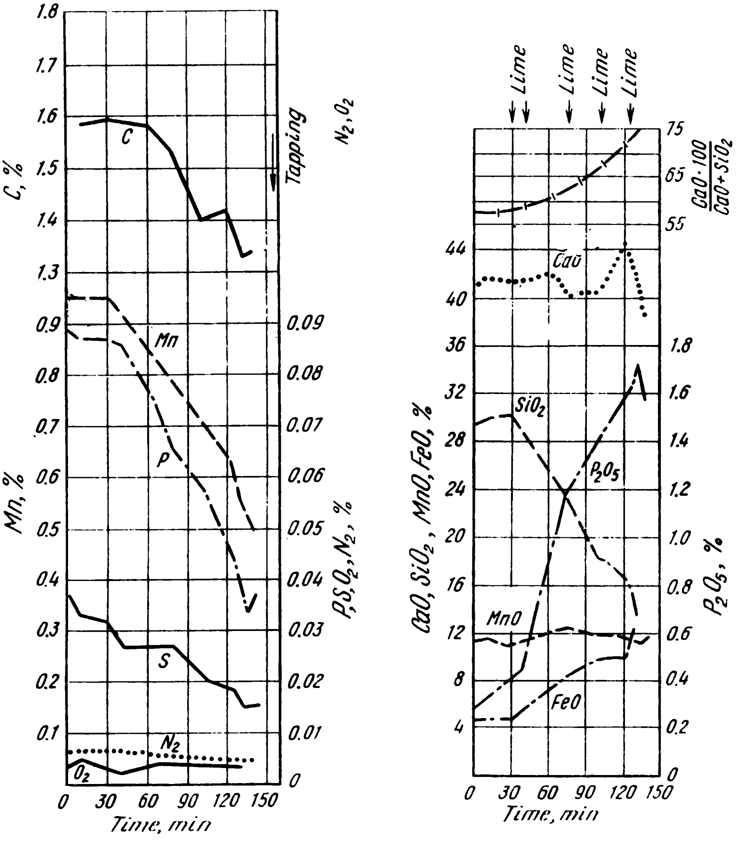


Fig. 117. Oxidation of impurities in the basic bath during the duplex process

The acid furnace is operated by the silicon-reducing process, with the silicon reduced by the end of the heat to 0.30 per cent. Manganese is also reduced owing to the high MnO content of the slag.

An essential drawback of the duplex process as described here is the difficulty of synchronizing the operation of the two furnaces, which means in practice a big drop in their productivity.

An acid steel differs from basic in better quality. The content of gases in it is insignificant; for instance, medium carbon acid steel contains roughly 0.004-0.009 per cent

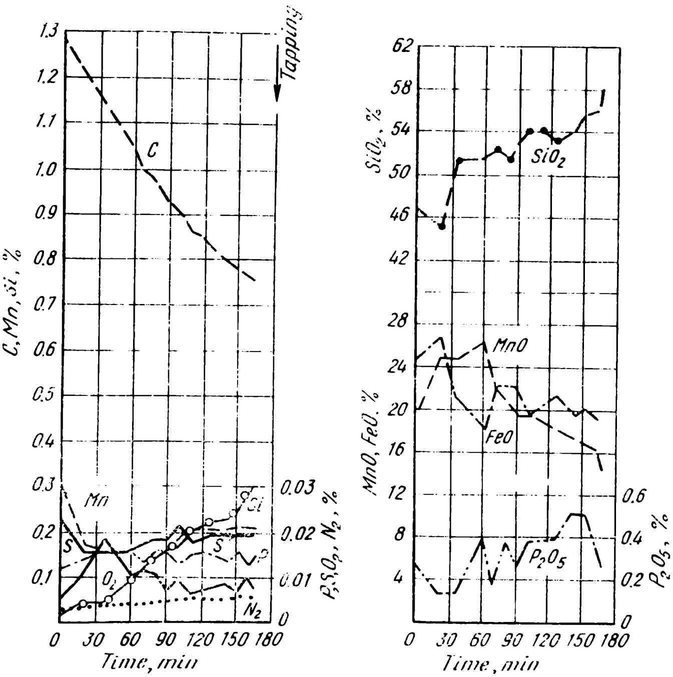


Fig. 118. Oxidation of impurities in the acid bath during the duplex process

oxygen, 0.0010-0.0015 per cent nitrogen, and 2-4 cm^3 hydrogen per 100 g of metal. This may be explained by a pure metallic charge and protective properties of the slag. It is also low in nonmetallic inclusions owing to an appreciable decrease in the number of sulphide inclusions, which again can be attributed to the purity of the charge materials. Oxide inclusions are fewer than in basic steel since they are readily picked up by the acid slags.

The residual silicate inclusions are most often round in shape and therefore are less detrimental to the quality of steel.

Owing to its improvements, the basic open-hearth process is now employed with success for making some critical grades of steel which were formerly made only in acid furnaces. The amount of steel produced in acid open-hearth furnaces is now not more than 2-5 per cent of the total production of open-hearth steels.

Chapter Sixteen

OPEN-HEARTH CONVERSION OF HIGH-CHROMIUM CHARGES

When oxidized, chromium may form CrO_3, Cr_2O_3 or CrO. In a basic open-hearth furnace, only CrO can exist in the metal, and only Cr_2O_3 in the slag, since CrO_3 decomposes at a low temperature (250°C) by the reaction $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2 - Q$.

In the slags of the acid open-hearth process, chromium is present mostly as CrO, forming fusible compounds with SiO_2.

The oxidation of chromium follows the reaction

$$[Cr] + (FeO) = (CrO) + [Fe]$$

Using the equilibrium constant of this reaction, the distribution of chromium can be determined by the equation

$$\frac{(Cr)}{[Cr]} = K_{Cr}\frac{(Fe)}{100} = K'_{Cr}(Fe)$$

from which it follows that the distribution coefficient (Cr)/[Cr] is proportional to the iron content of the slag. The highest oxide Cr_2O_3 is formed in the acid process only in an insignificant quantity through oxidation of CrO to Cr_2O_3 in the slag.

In basic slags, chromium is present as Cr_2O_3 or $(FeO)\cdot(Cr_2O_3)$, i.e., chromite, which forms by the reaction

$$2[Cr] + 4(FeO) = (FeO\cdot Cr_2O_3) + 3[Fe]$$

Iron chromite separates as an excessive phase, and therefore its activity is unity. The equilibrium constant can then be written as

$$K''_{Cr} = [Cr]^2(FeO)^4$$

whence

$$[Cr] = \sqrt{\frac{K''_{Cr}}{(Fe)^2}}$$

i.e., the concentration of chromium in the metal decreases proportional to the square root of the iron content of the slag.

As has been found from numerous experiments, the distribution coefficient for chromium, $\eta_{Cr} = \%\,(Cr) : [Cr]$, is higher in the basic process than in the acid, which is linked with the appreciably higher content of free ferrous oxide in the basic slag and with the effect of the basicity of the latter.

The final equation of oxidation of chromium, assuming that iron cations constitute an appreciable part of the total number of cations present in the slag, will be

$$2[Cr] + 4(FeO) = (FeCr_2O_4) + 3[Fe] \qquad (a)$$

For the basic process, where calcium cations play the leading part among Fe, Mn, Mg and Ca cations, the final equation of chromium oxidation will be

$$2[Cr] + 3(FeO) + CaO = (CaCr_2O_4) + 3[Fe] \qquad (b)$$

The equation of equilibrium of reaction (a) is of the form

$$K_{Cr_1} = \frac{(a_{FeCr_2O_4})}{[\%\ Cr]^2\,(a_{FeO})^4}$$

$$\log K_{Cr_1} = \frac{80{,}940}{T} - 41.30$$

and that of reaction (b) is

$$K_{Cr_2} = \frac{(a_{CaCr_2O_4})}{[\%\ Cr]^2\,(a_{FeO})^3\,(a_{CaO})}$$

Numerical values for the latter equation have not yet been found. It follows from the equations that

$$\frac{(a_{FeCr_2O_4})}{[\%\ Cr]^2} = K_{Cr_1}\,(a_{FeO})^4$$

and

$$\frac{(a_{CaCr_2O_4})}{[\%\ Cr]^2} = K_{Cr_2}\,(a_{FeO})^3\,(a_{CaO})$$

Thus, the oxidation of chromium in either acid or basic baths will be speeded up with an increase of the activity of ferrous oxide in the slags (Fig. 119) or a decrease of the temperature of the bath (K_{Cr_1} and K_{Cr_2} increase with decreasing temperature since the reactions are exothermic).

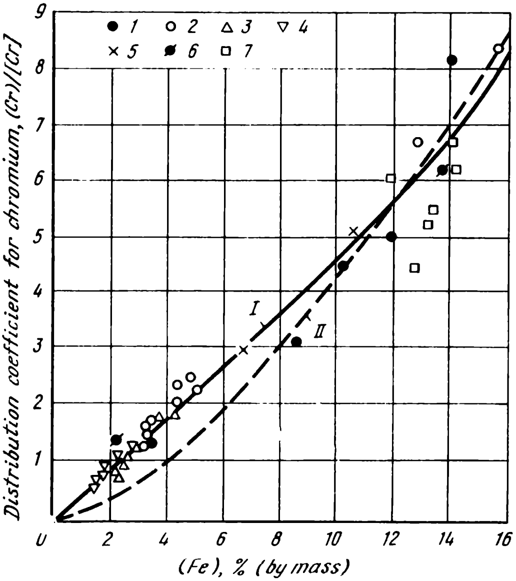


Fig. 119. Distribution coefficient for chromium as a function of iron content in (*I*) acid and (*II*) basic slags

1—0.07-0.14% Mn; *2*—0.42-0.63% Mn; *3*—0.69-1.05% Mn; *4*—1.2-1.4% Mn; *5*—reduction of chromium from slag; *6*—fluidizing of slag with lime; *7*—addition of carbon to metal

The oxidation of chromium in the basic process will occur more intensively since the reaction is accelerated by the activity of CaO; this is confirmed by experimental data.

Figure 120 shows the dependence of the distribution coefficient for chromium on slag basicity, and Fig. 121, its dependence on temperature.

Figure 122 shows the dependence of the Cr distribution coefficient on the silicon content of the liquid bath. In the basic process the silicon is oxidized fully by the moment of meltdown of the bath, while manganese still remains in the metal during the subsequent periods of the heat. A study has been carried out into the distribution of chromium at different concentrations of manganese in the metal and of manganous oxide in the slag. Figure 123 shows that the oxidation of chromium slows down as the concentration of manganese in the metal increases. This effect of Mn for the acid and basic processes is shown in Fig. 124. With an increase of the coefficient of distribution of manganese between slag and metal, the oxidation of chromium will slow down in the basic process and even almost stop in the acid process.

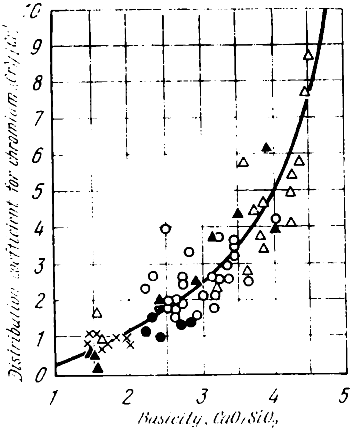


Fig. 120. Distribution coefficient for chromium as a function of slag basicity

It follows from what has been said above that for the oxidation of chromium to proceed, the bath must be low in silicon and manganese. Let us consider an example of the acid open-hearth process in which the activities of ferrous and manganous oxides in the slag are very low. As can be seen from Fig. 122, with 0.2 per cent Si present in the bath and its temperature of 1600-1640°C (Mn concentration in the bath is conditionally assumed to be low), the maximum possible coefficient of chromium distribution is $\eta_{Cr} = (\% \text{Cr}) : [\% \text{Cr}] = 2.1$, which is indicative of the fact that some of the chromium introduced with alloy scrap still remains in the bath.

Let us consider another example when the charge contains 1.2 per cent chromium and the bulk of slag formed in the furnace is 8 per cent (of the metallic charge). To find the content of chromium in the metal on tapping, we write the

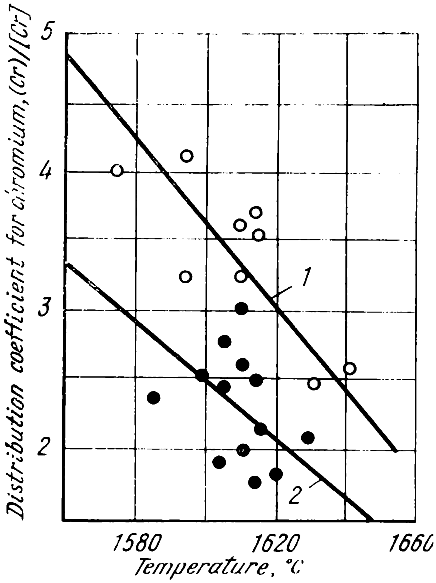


Fig. 121. Distribution coefficient for chromium as a function of metal temperature

1—over 7.5% (Fe); 2—below 7.5% (Fe)

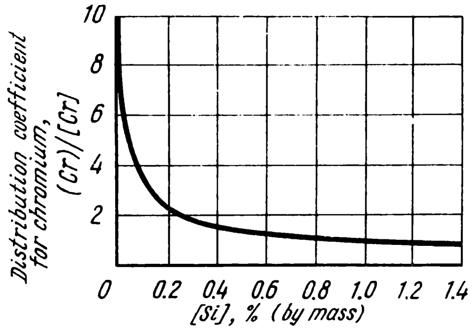


Fig. 122. Distribution coefficient for chromium as a function of silicon content of metal upon meltdown at 1600-1640°C

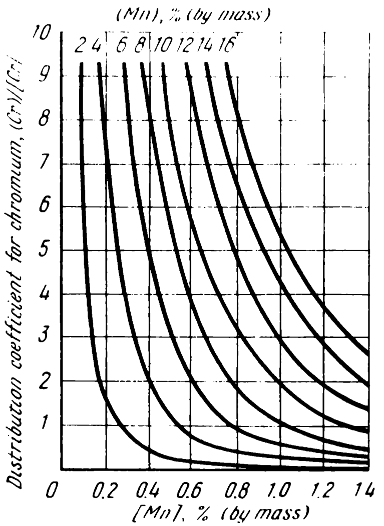


Fig. 123. Distribution coefficient for chromium as a function of manganese content of metal and slag upon meltdown

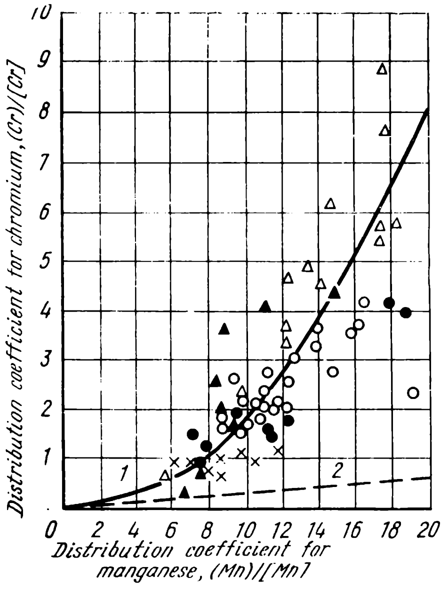


Fig. 124. Dependence of the distribution coefficient for chromium on (Mn) : [Mn] ratio

1—for basic slags; 2—for acid slags

balance equation of chromium concentrations in the metal and slag:

$$\% \mathrm{Cr}_{ch} = [\% \mathrm{Cr}] + (\% \mathrm{Cr}) \cdot B$$

where $\% \mathrm{Cr}_{ch}$ = chromium content in the charge, per cent of the mass of metal

$[\% \mathrm{Cr}]$ = chromium content in the metallic bath

B = bulk of slag, per cent of the mass of metal

Since $(\% \mathrm{Cr}) = \eta_{\mathrm{Cr}} [\% \mathrm{Cr}]$, it follows from the balance equation that the content of chromium in the metal is

$$[\% \mathrm{Cr}] = \frac{\% \mathrm{Cr}_{ch}}{1 + \eta_{\mathrm{Cr}} B} = \frac{1.2}{1 + 2.1 \times 0.08} = 1.03\%$$

i.e., 1.2 — 1.03 = 0.17 per cent Cr or 14 per cent of its total content in the charge will pass to slag. But if the chromium content of the metal is to be lowered to 1.0 per cent, the silicon-reducing process should be abandoned for the active process, in which, as is known, lime and mill scale are added to the slag to increase the content of iron oxides in the latter, i.e., we must increase the coefficient of chromium distribution to

$$\eta_{\mathrm{Cr}} = \frac{(\% \mathrm{Cr})}{[\% \mathrm{Cr}]} = \frac{\% \mathrm{Cr}_{ch} - [\% \mathrm{Cr}]}{[\% \mathrm{Cr}] \cdot B} = \frac{1.2 - 1.0}{1.0 - 0.08} = 2.5$$

This value corresponds to 0.18 per cent Si in the bath, i.e., a slight amount of silicon must be additionally oxidized so as to have not more than 0.18 per cent of residual silicon in the metal (see Fig. 122). This can be done by blowing the bath with oxygen for a short time.

As may be concluded from the analysis made above, the acid open-hearth process is suitable for reducing chromium, especially when the operation is done by the passive silicon-reducing process.

Quite different physico-chemical phenomena will be observed in a basic open-hearth furnace during the interaction between the metal and the slag in which the activities of CaO and FeO are high. On the one hand, in the intensified operation of modern basic open-hearth furnaces with the supply of oxygen into the flame and the bath, there remains no silicon in the bath by the moment of meltdown and the metal is low in the residual manganese (0.10-0.15 per cent) already at an early stage of the heat, and still lower in the operation with a low-manganese pig iron. On the other hand, the slags are rich in FeO (14-22 per cent) and their basicity reaches 2.5-3.0 during the finishing period. Under such conditions it is apparently difficult to retain chromium in the metal.

Let us find the residual chromium in the metallic bath for the following conditions: the chromium content of the charge is 1.0 per cent; the bulk of slag in the furnace, 15 per cent of the metallic charge; and the slag basicity, 3.0.

Referring to Fig. 120, the slag basicity of 3.0 gives the coefficient of chromium distribution $\eta_{Cr} = 2.5$. The residual concentration of chromium in the bath is found by the equation

$$[\%\,\mathrm{Cr}] = \frac{\%\,\mathrm{Cr}_{ch}}{1+\eta_{Cr}\cdot B} = \frac{1.0}{1+2.5\times 0.15} = 0.72 \text{ per cent}$$

But this value may be incorrect, since the metal is simultaneously under the action of ferruginous slags. Let us check the probable content of chromium in the bath for the same initial data, but using the coefficient of chromium distribution from Fig. 119 for the case when the slag contains 15 per cent Fe. Then, $\eta_{Cr} = 8$ and the residual chromium in the metal is

$$[\%\,\mathrm{Cr}] = \frac{\%\,\mathrm{Cr}_{ch}}{1+\eta_{Cr}\cdot B} = \frac{1.0}{1+8\times 0.15} = 0.45 \text{ per cent}$$

Thus, it is impossible to retain chromium in the bath because of the action of high-oxidizing slags. The latter result is also somewhat high, but close to the actual values observed in practice. It is probable that the loss of chromium is influenced by slag basicity and the formation of spinels of the type $(\mathrm{Fe, Mg})\mathrm{O}\cdot(\mathrm{Cr, Al, Fe})_2\mathrm{O}_3$.

It follows from the calculation made above that the chromium of the charge is oxidized in the open-hearth furnace and passes to slag. The residual content of chromium in the bath can be roughly determined by the equation

$$\frac{[\%\,\mathrm{Cr}]}{\%\,\mathrm{Cr}_{ch}} = \frac{1}{1+\eta_{Cr}\cdot B}$$

from which it is seen that the chromium content of the metal will increase with a rise in the chromium content of the charge, decrease in the distribution coefficient, and lowering of the bulk of slag. All other things being the same, the chromium content of the metal will grow at higher temperatures of the heat with the slags of low oxidation power and basicity.

By controlling these factors, i.e., the bulk and composition of the slag and the temperature of the process, it is possible to obtain the desired coefficient of distribution of chromium between slag and metal.

Conversion of high-chromium charges is always linked with certain difficulties owing to the formation of Cr_2O_3 (melting point 2280°C) or high-melting chromite $FeO \cdot Cr_2O_3$ (melting point 2112-2180°C). Even at comparatively low concentrations of Cr_2O_3 in the slag (5-8 per cent), chromite and iron particles begin to segregate from the solution, the slag becomes heterogeneous and viscous, and poorly conducts the heat from the flame, so that the melt in the open-hearth furnace becomes almost impossible. It is then considered reasonable to prerefine high-chromium pig iron, for instance, in a Bessemer converter so as to lower its chromium content, before using it in an open-hearth furnace.

As has been given earlier, Bessemer conversion of pig iron containing 2.2-3.6 per cent Cr and 0.8 per cent Ni is used with success at the Orsko-Khalilovsky integrated works to make semiproduct with the same content of nickel and 0.2-0.6 per cent Cr and 2.4-3.0 per cent C. The semiproduct together with steel scrap is then treated for steel in basic open-hearth furnaces. The pig iron-to-scrap ratio of the charge is fully governed by the specified nickel content of the final steel.

In view of the high content of phosphorus in the semiproduct (0.35-0.40 per cent), the operation is carried out with repeated slagging-off during melting and refining, new slags being formed by adding lime and bauxites. The slags are fluidized by additions of bauxites, fluorspar, and glauconite-carbonate ore. Apart from the usual components, the slags contain 1.5-2.5 per cent Cr_2O_3 and 2.5-7.0 per cent P_2O_5.

The bath after meltdown contains 0.01-0.05 per cent Mn, 0.02-0.06 per cent P, 0.05-0.08 per cent Si, 0.15-0.25 per cent Cr, and 0.45-0.80 per cent Ni. The final metal prior to deoxidation has 0.01-0.03 per cent P, 0.1-0.2 per cent Cr, and 0.45-0.80 per cent Ni.

Conversion of high-chromium scrap in open-hearth furnaces is done with wide usage of metal rejects of the same steel from rolling mills, for it is profitable to utilize the nickel contained in the rejected metal. The operation may be done by either chromium-oxidizing or chromium reducing processes.

CHROMIUM-OXIDIZING PROCESS FOR CONVERSION OF HIGH-CHROMIUM CHARGES

As has been established, the reduction of chromium from the slag is accompanied by an increase of the nitrogen concentration in the metal. For that reason it is advisable to limit the amount of chromium to be reduced in a basic furnace to 0.34 per cent. In acid furnaces, chromium may be allowed to reduce to higher concentrations, since the nitrogen content of steel is not increased in the acid process.

In view of the difficulties linked with the conversion of high-chromium stock and also because of the formation in the bath of thick heterogeneous slags rich in chromium oxides, and the adverse effect of chromium as a nitride-forming element, a process based on oxidation of chromium has found use in many countries. It consists in a quick and possibly full oxidation of the chromium (and also the phosphorus) of the charge and in removal of quite a large amount of slag from the bath. Basic open-hearth furnaces are used with success for the purpose. The operation is done with one or two slaggings-off, the new slags being formed by adding lime and bauxites. The final slag is low in phosphorus and chromium oxides and the metal under it usually contains not more than 0.2 per cent Cr and 0.03 per cent P. The finishing of the bath in the process is carried out, as usual, under the final slag having not more than 8-10 per cent FeO, 6-8 per cent Al_2O_3 and a basicity of about 3. An essential drawback of the chromium-oxidizing process is that much time is spent for slagging-off and formation of new slags; this can be compensated for by blowing the bath with oxygen, The problem of converting high-chromium metal becomes more and more complicated, since chromium-containing grades of steel grow in number, and therefore rejected metal and scrap become more and more contaminated with chromium.

CHROMIUM REDUCING PROCESS FOR CONVERSION OF HIGH CHROMIUM CHARGES

This process can provide a large economic effect owing to a high degree of utilization of the chromium, nickel, and manganese of the charge. The main difficulties are the possible reduction of phosphorus from the slag together with chromium and a higher nitrogen content of the metal because of the presence of chromium in the bath. The following principles should be observed to save to a maximum the chromium contained in the charge:

To make medium-carbon steel, the charge should be calculated so that the carbon content of the first test sample can be approximately 1.1 per cent, with a silicon content in the charge 0.4-0.5 per cent. The charge should be melted as fast as possible. The bulk of slag should be minimized so as to lower the amount of chromium passing to it. For that reason, the amount of lime in the charge should be limited to 2.0 per cent, with a total of 4.5-5.5 per cent (of the metallic charge) for the heat.

The low basicity of the slag at the beginning of boil (1.4-1.8) should be raised to 2.0-2.5 by the end of the heat, with the iron content in the slag not exceeding 8 per cent. The operation is done without slagging-off.

Experiments have shown that the calcium phosphates in the slag are quite stable during the reduction of chromium, provided that the slag basicity is raised to 1.8-2.0 and the process run at a high temperature. This dephosphorization accomplished simultaneously with chromium reduction has been termed 'hot dephosphorization'. Slagging-off is done but occasionally and only in the later period when the slag becomes sufficiently low in chromium. A new slag is formed by adding lime and iron ore. Since the bulk of slag is not large, its basicity can be raised rapidly by adding small amounts of lime.

Because of the high utilization of the chromium of the charge (75-85 per cent), this process can be considered very effective.

The purely carburizing chromium-reducing process developed at one of the works abroad presents interest. The charge was 98 per cent high-chromium return scrap, 1.5 per cent mirror iron, and 0.5 per cent ferro-silicon (45-%). The first test sample on meltdown had 0.5-1.0 per cent Si. The basicity of the slag, which was not high at the initial stage of the heat, was then increased to 2.5-3.0. With a low loss of chromium in the slag, dephosphorization was quite deep and the steel had a rather low sulphur content.

The processes described above can only be carried out in furnaces of high thermal capacity and with the charge materials very pure from phosphorus and sulphur.

Iron ores from certain mines in the USSR are used for making high-chromium pig irons containing up to 2.8 per cent Cr, 2.5 per cent Ni, and 0.34 per cent P. The following version of the chromium-reducing process has been developed for treating these pig irons:

(1) high-temperature conditions are maintained during the whole course of the operation, from charging to tapping;

(2) the charge is calculated so that the surplus carbon with the hot run of the furnace does not exceed 0.5-0.7 per cent; the content of silicon in the charge varies between 0.5 and 0.6 per cent, and that in test samples on meltdown, between 0.05-0.20 per cent; the concentration of manganese is at least 1.0 per cent, and that of chromium, not more than 1.2-1.3 per cent (for silica-roof furnaces); for furnaces with the roof and ports made of magnesite-chromite brick, the content of chromium in the charge may be increased to 1.8 per cent; the concentration of phosphorus does not exceed 0.1 per cent, and of sulphur, 0.06 per cent;

(3) to provide slag conditions ensuring maximum retention of chromium in the metal on meltdown, the amount of bauxites to be charged is increased to 1.5-2.0 per cent with 6-8 per cent limestone or 5-6 per cent lime added; this ensures 8-12 per cent FeO and 9-12 per cent Al_2O_3 in the slag by the moment of meltdown and a fast growth of slag basicity up to 2.0-2.5; the latter reaches 2.5-3.0 during the period of pure boil.

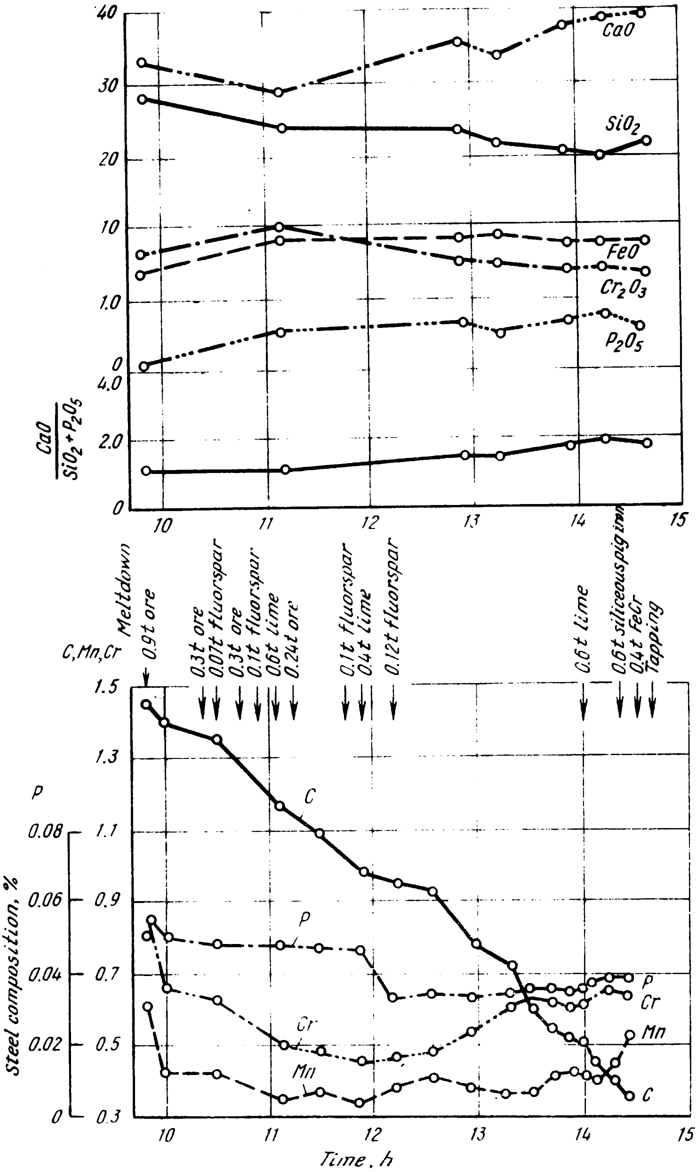


Fig. 125. Variations of the contents of impurities in the bath and of oxides in the slag in a melt by the chromium-reducing process

During the pure boil and after the maximum possible reduction of chromium and oxidation of phosphorus, the initial slag is skimmed off. In that way the processes of dephosphorization and chromium reduction are separated quite fully.

Manganese reduction from slag usually occurs at the same time as chromium reduction.

Figure 125 shows variations in the contents of impurities in a heat run by the chromium-reducing process. Ladle analysis of the metal was as follows: 0.40 per cent C, 0.63 per cent Mn, 0.27 per cent Si, 0.037 per cent P, 0.019 per cent S, 0.18 per cent Ni, and 1.00 per cent Cr. The nitrogen content of the steel did not exceed that of the common open-hearth steel (0.002-0.008 per cent) for the chromium content of 0.88-1.61 per cent in the charge.

Chapter Seventeen

MODERNIZATION OF OPEN-HEARTH STEELMAKING

The open-hearth process, though being gradually displaced by the oxygen converter process, still plays the leading role in the steel manufacture in the USSR. Using this process, enormous stocks of steel scrap and roll mill rejects are converted into quality and high-quality steels.

The process is continuously modernized and improved on the basis of the newest achievements in modern engineering and technology.

One of the methods for increasing the productivity of open-hearth furnaces is to use technical oxygen. This method, especially when oxygen is used to blow the liquid bath, appreciably speeds up the steelmaking process, shortens the individual melt periods and the tap-to-tap time as a whole, increases furnace productivity, and saves fuel. But this powerful tool is only effective when all the sections of the production process are prepared for passing through larger amounts of charging and other materials and for removal of waste products.

This method of intensified steelmaking requires large-size charging boxes for rapid charging of specially prepared scrap, powerful charging machines, quick pouring of hot metal, and an ample supply of technical oxygen at the works.

The use of oxygen increases dust formation, so that the slag chambers must be cleaned in shorter intervals (after 200-250 heats) and the checkerwork must be blown with steam or washed with water under pressure. Water must be sprayed in the slag pockets (at a rate not less than 0.5 m^3/min) in order to prevent smelting of the checkerwork.

When gaseous oxygen is blown into the bath, the amount of iron ore in the charge reduces substantially and, in addition, the heat runs with an increased oxidation loss of iron, all this resulting in a lower yield of steel. But economic calculations show that this method is effective in increasing appreciably the productivity of furnaces.

With the scrap-and-ore process carried out in furnaces with single- or two-channel ports, oxygen is supplied into the flame by means of a combined burner; in furnaces with three-channel ports it is supplied via tuyeres arranged at the side walls of the gas port.

In shops where conditions are ensured for rapid charging of scrap, the furnaces are provided with short-length stationary gas-oxygen burners mounted in their roofs. The burner consists of three concentric pipes, the inner pipe serving to supply oxygen, the intermediate one to supply gas, and the outer pipe to supply cooling water. These burners are put into operation during charging of large-size scrap.

Such burners are also used with success in the pig-and-scrap process. The productivity of furnaces in that case increases by 22-27 per cent and the consumption of fuel reduces by 12 per cent. But the use of such burners increases the wear of the furnace lining.

The productivity of an open-hearth furnace can be raised by increasing its capacity. By rebuilding small-size furnaces into larger ones their productivity can be increased by a factor of 1.6-1.8. This method is employed at all steelmaking works in the USSR.

The productivity of an open-hearth furnace can be increased by accelerating the processes of dephosphorization and desulphurization, for which purpose powdered lime together with other materials are blown in the melt. In melts with a low carbon content this may be done by blowing in graphite, coke breeze, etc.

Much attention is paid to the methods of deoxidation and alloying of steel outside the furnace. By using these methods, it is possible to increase the productivity of furnaces and reduce substantially the loss of deoxidants, and also to purify the metal more deeply from the products of deoxidation owing to the effect of convective mixing of metal in the ladle. These measures, just as vacuum treatment of the steel before deoxidation, treatment of the liquid metal with argon, and processing with synthetic slags, result in an appreciable improvement of the quality of steel.

INCREASING THE LIFE OF INDIVIDUAL ELEMENTS OF FURNACE LINING

In furnaces operating with an intensive oxygen blowing, it is advisable to increase the height of the main roof, the area of the flame window and vertical channels, the volume of slag chambers, and the size of cells in the regenerators. Periodical blowing of the dust from the outside surface of the main roof by means of compressed air or superheated steam and guniting of the inner surface of the main roof, end walls of the ports and the walls of the reaction chamber can increase the life of the lining of the main roof and reaction chamber. Guniting can also be used for patching worn-off places in the roof. Washing of the checkerwork with water (under a pressure of 10-12 at) is started upon making 30 heats after a cold repair and is then repeated every 7-10 days. Dust from beneath the checkerwork is blown out by compressed steam (10-20 at).

In furnaces of the Maerz-Boelen type, the front and rear walls above the slag line are made of refractory blocks. This shortens the time of furnace repair, since blocks can be prepared in advance. Some hot repairs are also made by using blocks. The walls in this type of furnace are made inclined, so that the span of the roof becomes substantially shorter. This improves the conditions of radiant heat transfer from the lining to the bath, as well as increases the life of the roof. The productivity of such furnaces is higher and the consumption of fuel and refractories lower than with ordinary open-hearth furnaces.

Some advantages of this type of furnace are also used with success for operation by the pig-and-scrap process. In this case the furnace is repaired by using charging machines of the crane type. In addition, blocks are handled and laid by means of the overhead cranes for waste-removal.

In shops with large-capacity furnaces run by the scrap-and-ore process, this operation is done by means of iron-pouring cranes. But strong foaming of the slag causes rapid wear of the blocks, while common fettling of the furnaces of this type is linked with some difficulties. For that reason the expediency of the use of blocks in large-size furnaces requires further checking. Until then, measures must be found to prevent premature wear, spalling and smelting of roof refractories. Increasing the height of the main roof is an effective means for protection against slag splashing, which is especially important when the furnace is run with oxygen blowing. One of the causes of spalling of roof bricks is penetration of melt dust therein. As has been found, magnesite-chromite roof bricks can swell in the presence of some kinds of spinel. The greatest swelling is observed during the interaction of magnetite $FeO \cdot Fe_2O_3$ with chrome spinel. Spalling can also be caused by thermal shocks to which the roof is subjected. For instance, it is supposed that during the repair of the hearth by the new method the temperature of the roof drops to 1100°C owing to a reduced fuel supply during the repair (this is done to reduce the amount of magnesite powder carried off with the outgoing gases). This method of repair shortens the time of repair to 0.55 per cent of the total operating time, but increases the wear of the roof through thermal shocks.

Further search for new high-refractory materials and improvement of measures for prevention of premature roof wear may prove effective for increasing the life of the main roof of open-hearth furnaces.

FUEL, THERMAL LOAD, AND AUTOMATIC CONTROL OF THERMAL CONDITIONS OF FURNACE OPERATION

The last decade has opened the possibility of a wide use of natural gas for firing open-hearth furnaces with single- and twin-channel ports, fuel oil (15-25 per cent of the heat produced) being added to the gas in order to increase radiance and stability of the flame.

In furnaces with three-channel ports, natural gas is preliminarily carburized by small additions of fuel oil or the firing proceeds on the principle of self-carburization of the fuel.

The use of natural gas and fuel oil for firing open-hearth furnaces opens a possibility for modernizing the furnace design and increasing the area of the hearth. For instance, when a 200-225-ton furnace was converted to natural gas firing, its three-channel ports were replaced with single-channel ones and the bath was widened by changing the profile of the rear wall, so that the area of the hearth was enlarged from 67 to 95 m^2 (Fig. 126) and the charging capacity was increased to 400-450 t. Owing to the removal of the partitions in the slag chambers and regenerators and the replacement of arch roofs with flat suspended roofs, the volume of the slag chambers was increased from 215 to 292 m^2 and that of the checkerwork, from 304 to 370 m^3. These improvements made it possible to increase the thermal loads from 29×10^6 to 39×10^6 kcal/h owing to firing of natural gas and fuel oil and to intensify fuel combustion with oxygen during charging.

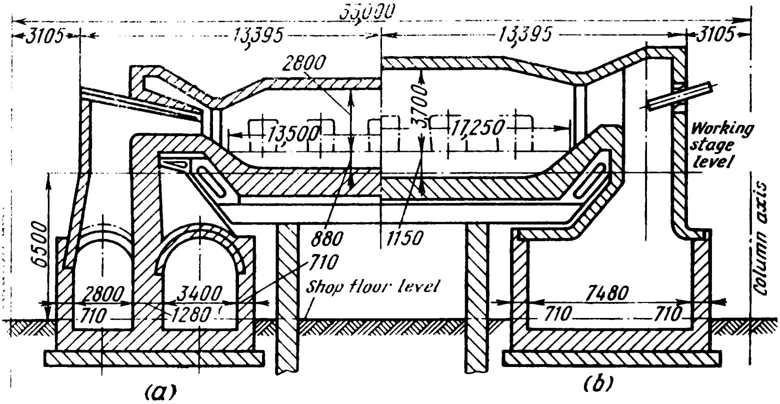


Fig. 126. Reconstruction of 220-ton furnace for a capacity of 400 tons
a—old furnace; *b*—reconstructed furnace

Of large importance for self-carburization of natural gas is the presence of unsaturated hydrocarbons of types of C_2H_4 or C_2H_2 in the molecules of which the C : H mass ratio is more than six. Such hydrocarbons can form carbon-black particles that make the flame radiant. Hydrocarbons in which this ratio is less than six are less efficient in this respect. The situation is remedied somewhat by fuel oil which upon burning also forms solid particles of coke and the flame becomes radiant (the C : H ratio for fuel oil is 8.15).

When firing furnaces with a gas mixture (blast-furnace plus coke-oven gas), it must be kept in mind that the content of carbon black in the gas increases with an increase of the temperature of its heating in regenerators. With the gas mixture of a calorific value of 2300 cal/m^3 heated up to 1150°C, as much as 70 g of carbon black per m^3 is formed, which is quite sufficient to make the flame radiant without resorting to flame carburization with fuel oil. With a higher proportion of coke-oven gas in the mixture and therefore with its higher calorific value, the proportion of carbon black formed after heating in regenerators is even more.

With any kind of fuel used, it must be burned so as to form a long sharp flame moving with a high rate at the surface of the bath. Under such conditions the proportion of heat transferred to the bath by convection increases noticeably. An effective method for shaping the flame is to blow in compressed air through the end face of the gas port or from its sides. This increases the energy of fuel flow, intensifies heat- and mass-transfer processes, and improves the oxidizing ability of the flame.

When selecting thermal loads and the shape of flame, one must keep in mind that higher thermal loads during charging can be recommended only for large-size scrap with a high speed of its charging. This should not be done with light-weight scrap, because it melts quickly and becomes excessively covered with scale, which may result in bath foaming after the pouring of pig iron in the scrap-and-ore process or in bath chilling in the pig-and-scrap process. In both cases the period of melting and therefore the tap-to-tap time become longer. High thermal loads must also be avoided during charging of loose materials (iron ore, limestone, lime, bauxite, etc.) having poor thermal conductivity, since this may cause quicker wear of the roof and walls of furnaces.

Automatic control of thermal conditions of furnaces is of very high importance for increasing their productivity. At present, the main thermal parameters are controlled independently: roof temperature (measured by a pyrometer probe) is controlled by varying the flow rate of fuel; air excess factor (measured by an excess oxygen analyzer, namely an alpha-indicator) is controlled by varying the flow rate of oxygen and air supplied to the flame; the temperature of the checkerwork is controlled by cooling the outgoing gases in the slag chambers by means of sprayed water; the pressure in the reaction chamber, by varying the draught and the flow rate of compressed air; valve reversal is made in the intervals specified for each period of the heat.

The use of new kinds of high-calorific fuel and the application of oxygen for intensified burning of fuel and for bath blowing are inconceivable without automatic control of thermal conditions. Automatic control of furnace operation reduces both the tap-to-tap time and fuel consumption approximately by 5-7 per cent.

INSTALLATION OF OXYGEN CONVERTERS IN OPEN HEARTH SHOPS

Extensive research is now under way into the problem of replacement of open-hearth shops with oxygen converters in existing shops. A satisfactory solution would enable the existing equipment to be used in reconstructed shops and thus reduce substantially the capital expenditures of reconstruction.

As has been found through the results of this research, only top-blown converters of a comparatively small capacity can be installed in place of furnaces in the furnace bay of most shops. Larger converters, for instance, of a capacity of 180 tons, can be installed in the charge bay.

Figure 127*a* shows how an oxygen converter of a capacity of 70 tons can be installed instead of an open-hearth furnace in the shop building of a low height. The oxygen lance is handled by means of a cantilever crane. The gases from the converter are removed via a curved gas duct into the slag chamber, where they are afterburned in air and further cooled by water spraying. The gases are then fed for further cooling and dust cleaning into a dust-cleaning device.

At the end of the heat the lance is lifted but not withdrawn from the gas duct, the lance and the gas duct being moved

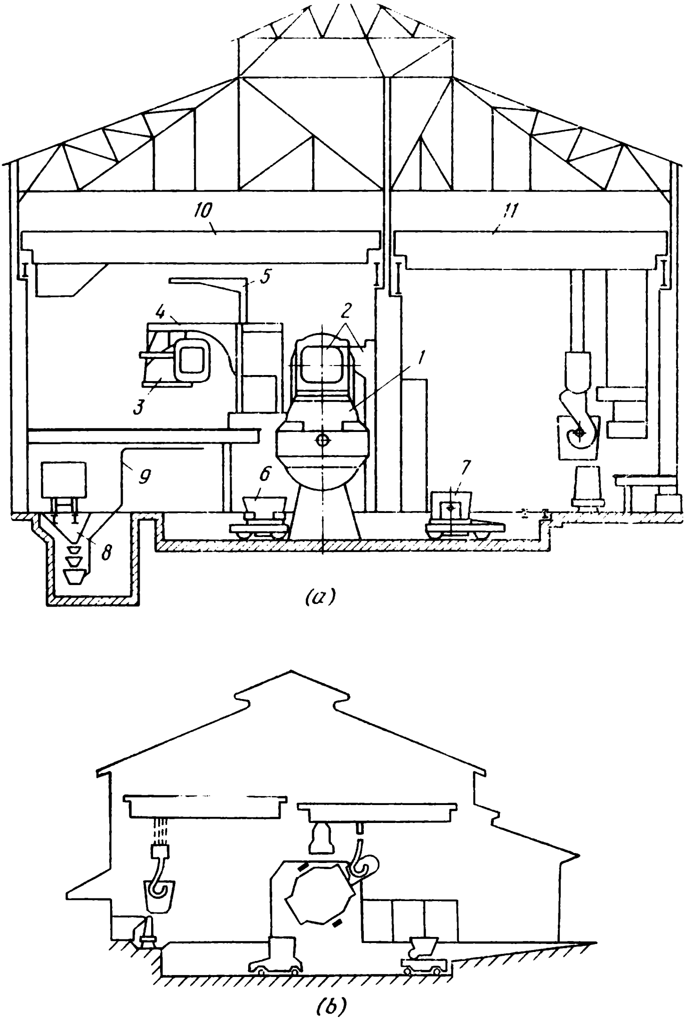


Fig. 127. Arrangement of converters in the building of an open-hearth shop

1—converter; *2*—removal and afterburning of gases; *3*—detachable water-cooled gas duct; *4*—cantilever crane; *5*—lance-handling cantilever crane; *6*—slag pot; *7*—teeming ladle; *8*—bunkers; *9*—pneumatic transportation of loose materials; *10*—iron-pouring crane; *11*—teeming crane aside by the cantilever crane. This makes it possible to reduce the height of the plant by 2 metres. Solid components of the charge are delivered and charged in shovel-type boxes handled by a charging machine.

A better solution has been found recently with the implementation of the Q-BOP process. For instance, in the open-hearth shop of one of the works in Fairfield, 12 open-hearth furnaces of a capacity of 210 tons will be replaced by bottom-blown oxygen converters. Two 180-ton converters have been already installed (Fig. 127*b*) and the shop operates using the former equipment for scrap charging, iron pouring, teeming, and waste removal*. Since the lance and upper bunkers are not needed in the process and since oxygen, protective gas and lime powder can be supplied from below, larger converters can be installed in the furnace bay of the open-hearth shop.

But, as will be seen from Fig. 127, sufficiently deep trenches must be provided under converters in both cases for ladle cars and slag carriers.

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* Iron and Steel Engineer, 1973, No. 10, pp. 37-43.

Chapter Eighteen

DEOXIDATION AND ALLOYING OF STEEL

1. VARIOUS METHODS OF DEOXIDATION

Oxygen is readily soluble in liquid pure iron but in solid iron its solubility is very insignificant. The common constitutional diagram of the Fe-O system shows the solubility of oxygen as a liquid or solid solution, without taking into account the oxygen present in the metal as various oxides (nonmetallic inclusions).

Since the quantity of inclusions in steel is related to the oxygen dissolved in molten metal, the smelter must carry out the heat so as to decrease the oxygen content of the liquid bath to a minimum at the end of the refining period.

Oxygen is present in molten iron in the form of either atoms interacting with iron atoms or anions O^{2-}. This means that when an oxide, for instance, FeO or MnO, interacts with the liquid iron, it passes into the solution as a cation of the element and an oxygen anion, i.e., Fe^{2+} (or Mn^{2+}) and O^{2-}, rather than as FeO or MnO.

Among iron oxides, ferrous oxide has the highest solubility in liquid iron, so that the solubility of oxygen in iron will be maximal when iron contacts ferrous oxide.

Pure iron, whose melting point is 1539°C, becomes more fusible as the oxygen concentration of the solution increases, the minimum melting point of 1524°C corresponding to an oxygen concentration of 0.16 per cent. With further increase of its temperature, iron dissolves more oxygen (in the form of [FeO]), as can be seen in Fig. 128.

The curve in that figure can be well described analytically as a temperature function of the maximum oxygen content of iron:

$$\log \% [O]_{\max} = -\frac{6320}{T} + 2.734$$

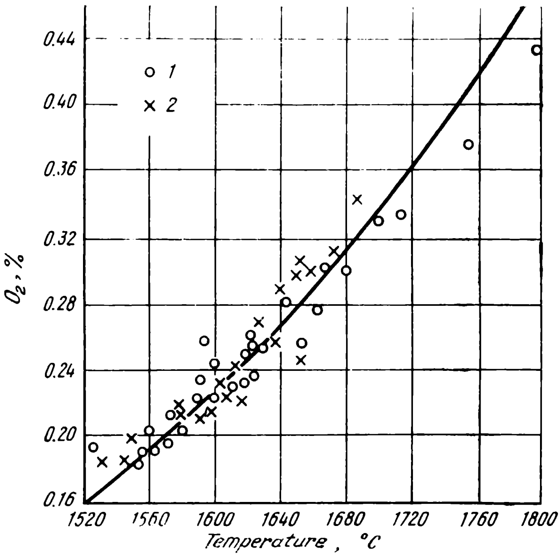

Fig. 128. Effect of temperature on solubility of oxygen in molten iron
1—data of one research; 2—data of another research

A similar relationship for solubility of oxygen in liquid iron is given by the Körber-Oelsen formula:

$$\% [O]_{max} = 0.131 \times 10^{-2} t\,°C - 1.77$$

or, recalculated to FeO by

$$[\% FeO]_{max} = 0.589 \times 10^{-2} t\,°C - 7.96$$

OXYGEN CONTENT OF MOLTEN BATH

The concentration of the oxygen dissolved in the liquid bath just after meltdown is low because the metal still contains many admixtures (silicon, carbon, manganese, etc.) in large concentrations. As these elements burn out in the course of refining, the concentration of the dissolved oxygen gradually increases and reaches its maximum when the bath has no silicon and is low in carbon.

A very pronounced dependence of the oxygen concentration on the carbon content indicates that carbon has an extremely high deoxidizing ability in molten metal at the temperatures of steelmaking. The reaction

$$[FeO] + [C] = [Fe] + \{CO\}$$

slows down as carbon concentration falls and the level of the dissolved oxygen rises (see Fig. 99), since the product of these concentrations becomes nearly constant.

The diagram in Fig. 99 clearly shows that the oxygen levels in production conditions exceed the values corresponding to equilibrium by 0.015-0.025 per cent, reaching absolute concentrations of 0.012-0.060 per cent when the carbon content of the boiling bath comes to 0.06-0.90 per cent.

In all steelmaking processes (except for the acid silicon-reducing process) the steel must be deoxidized after having been brought to the specified carbon content to make the dissolved oxygen inactive and prevent further oxidation of carbon.

Concurrent with deoxidation, the steel is alloyed to the specified analysis. But when rimming steels are produced, deoxidation in the furnace or ladle is intentionally made incomplete, and is continued in the mould through the action of a part of the residual carbon.

Four methods of deoxidation are employed in modern steelmaking: (1) by precipitation; (2) by diffusion; (3) by treating with synthetic slags; and (4) by vacuum degassing (usually done in the ladle).

PRECIPITATION DEOXIDATION

The principle behind precipitation deoxidation is to let a deoxidant (or scavenger) having a greater affinity for oxygen than iron interact with liquid iron to form an oxide-precipitate, i.e., to convert the homogeneous system (molten steel with oxygen dissolved in it) to a heterogeneous system (molten steel with oxides suspended in it). As the density of the precipitate is lower than that of the molten steel, it separates out from the metal, Precipitation deoxidation can be expressed by the following generalized reaction:

$$[\mathrm{FeO}] + [Me] \rightarrow (Me\mathrm{O}) + [\mathrm{Fe}]$$

It is obvious that the more $[Me]$ is introduced for deoxidation, the lower is the residual concentration of [FeO] in the steel.

Best results are obtained when the deoxidants dissolve quickly and the products of deoxidation rapidly separate from the metal and float up to be readily picked up by the slag (film of oxides).

Elements possessing a high deoxidizing ability (Si, Al, Ti, Zr, Ca, and rare earths) should be preferred as deoxidants. The preferred elements are the ones which form low-melting oxides, i.e., oxides capable of coalescing in the molten state and of passing as rapidly as possible into the slag zone. From the same considerations, the oxide formed should have the lowest possible density.

The various elements that are applicable as deoxidants in steelmaking may be arranged in a certain order according to the thermal effects they produce (Table 49). The oxides are arranged in the table in the order of their diminishing stability, which is characterized by the thermal effect required to form one mole of oxygen. As will be seen from the table, the same order is obtained when the oxides are arranged by their dissociation pressure.

In the steelmaking practice, Ca, Al, Zr, B, Ti, Si, and Mn are used as deoxidants, the commonest being Mn, Si, and Al.

Curves of the deoxidizing ability of silicon, manganese, and carbon at temperatures of 1450-1650°C, calculated from their equilibrium constants, are given in Fig. 129.

When silicon and manganese are introduced together into the bath, their oxides segregate from the solution as a liquid slag phase. The rate of their rise through the melt can be estimated by Stoke's formula, which expresses the resistance offered by a stationary viscous medium to the movement of small spherical bodies (under 100 μm in diameter):

$$v = K\frac{2}{9}\cdot\frac{g}{\eta}r^2(d_m - d_s)$$

where v = rate of rise, cm/s
K = form factor
g = acceleration due to gravity, 981 cm/s^2
r = radius of spherical particle, cm
d_m = density of liquid metal, g/cm^3
d_s = density of slag particle, g/cm^3
η = dynamic viscosity of liquid metal, g/cm·s (equal to 0.025 P for molten steel at 1595°C)

Table 49

Thermodynamic Characteristics of Selected Elements

Reaction	Standard thermal effect per mole O_2, cal	Logarithm of oxide dissociation pressure at 1727 °C
$2Ca + O_2 = 2CaO$	302,260	—22.2
$2Mg + O_2 = 2MgO$	291,600	—20.6
$^4/_3Al + O_2 = ^2/_3Al_2O_3$	262,466	—17.7
$Zr + O_2 = ZrO_2$	258,800	—16.4
$^4/_3B + O_2 = ^2/_3B_2O_3$	232,700	Not found
$Ti + O_2 = TiO_2$	225,700	—13.6
$Si + O_2 = SiO_2$	207,850	—13.3
$^4/_3V + O_2 = ^2/_3V_2O_3$	197,300	Not found
$2Mn + O_2 = 2MnO$	193,440	—11.5
$^4/_3Cr + O_2 = ^2/_3Cr_2O_3$	192,600	—10.2
$2Zn + O_2 = 2ZnO$	166,900	—8.0
$^4/_5P + O_2 = ^2/_5P_2O_5$	148,000	—7.0
$^2/_3W + O_2 = ^2/_3WO_3$	130,330	—5.0
$2Fe + O_2 = 2FeO$	128,860	—6.9
$^2/_3Mo + O_2 = ^2/_3MoO_3$	120,270	—4.0
$2Ni + O_2 = 2NiO$	116,600	—3.3
$2Co + O_2 = 2CoO$	115,000	—5.1
$^4/_3As + O_2 = ^2/_3As_2O_3$	104,330	—2.0
$4Cu + O_2 = 2Cu_2O$	86,000	—0.6

Since the density of deoxidation products for the temperatures of molten steel is not yet established, we will use the values obtained at 20°C (Table 50). As will be seen from the table, the deoxidation products of the commonest deoxidants have high melting points. These oxides obviously segregate from the melt as suspensions (solid particles) rather than as emulsions (liquid particles) and are therefore unable to coalesce. The danger of contaminating the steel with these inclusions is however much less than would be expected, because the conditions developed in the bath are favourable for the formation of oxides yielding more complex alloys having lower melting points, and mainly because the deoxidation products are never pure oxides of the deoxidant used.

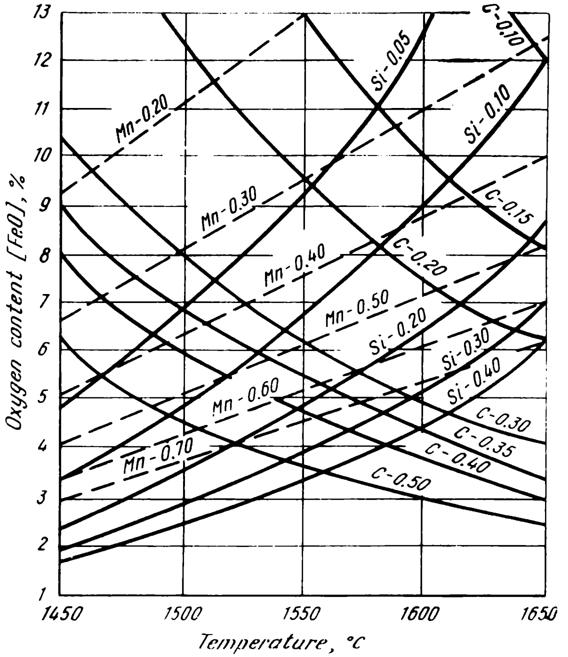

Fig. 129. Effect of temperature on deoxidizing ability of carbon, silicon, and manganese

Table 50

Melting Points and Densities of Oxides

Oxide	Melting point, °C	Density at 20 °C
Al_2O_3 (amorphous)	2045	3.85
Al_2O_3 (crystalline)	2050	
MnO	1785	5.40
SiO_2 (crystalline)	1713	2.40
TiO_2	1840	4.20
ZrO_2	2700	5.75

DEOXIDATION WITH MANGANESE

The conditions of refining of the bath, in particular, the elevation of temperature of the metal, are unfavourable for use of manganese as a deoxidant (the reaction $FeO + Mn \rightarrow MnO + Fe$ being exothermic). Manganese becomes an effective deoxidant, however, under conditions of lowering temperature in the furnace or on adding ferro-manganese into the running steel in the launder during tapping.

Though manganese has a lower deoxidizing ability than other elements employed in practice, it is used in making all grades of killed steel. Its restricted deoxidizing ability makes it indispensable in manufacture of rimming steels, provided that the ferro-manganese being used contains not more than 1 per cent Si.

The deoxidation reaction of manganese, which rapidly reaches equilibrium, may be regarded either heterogeneous at the metal/slag interface (which is more probable)

$$[Mn] + (FeO) \rightleftarrows [Fe] + (MnO)$$

or homogeneous in the bulk of molten metal

$$[Mn] + [FeO] \rightleftarrows (m\,MnO \cdot n\,FeO) + [Fe]$$

The deoxidation product is never pure manganese oxide (MnO), but an alloy of MnO and FeO since the residual FeO is rapidly dissolved in MnO in the reaction zone. The MnO/FeO ratio in the alloy depends on the temperature and manganese content of the bath.

The equilibrium constant of the reaction

$$[\mathrm{Mn}] + (\mathrm{FeO}) \rightleftharpoons [\mathrm{Fe}] + (\mathrm{MnO})$$

as a function of temperature is as follows:

$$\log K_{\mathrm{Mn}} = \log \frac{[\mathrm{Fe}](\mathrm{MnO})}{(\mathrm{FeO})[\mathrm{Mn}]} = \frac{6440}{T} - 2.95$$

The nature of the slag, i.e., the type of the process, whether acid or basic, has a substantial effect on the deoxidizing ability of manganese. Studies into the problem have shown that for acid slags the (MnO)/(FeO) ratio is several times as great as for basic slags with the same concentration of [Mn] in the steel, i.e., the steel under the acid slag contains less oxygen.

This means that with the same [FeO] concentration in the metal and an equal (FeO)/(MnO) ratio in the slags, other conditions being also equal, the deoxidizing effect produced on adding manganese to the bath will be different for acid and basic open-hearth furnaces; manganese is oxidized much more fully in the acid process than in the basic one. In other words, for the same charge of an acid and a basic furnace and the same addition of ferro-manganese, the metal in the acid furnace will be lower in manganese than in the basic one. The melter must keep this in mind to avoid tapping the metal that does not meet the specification.

Effect of temperature. Lowering the temperature is favourable for deoxidation with manganese, as is well shown in the diagram in Fig. 129. As can be seen, the deoxidizing ability of manganese rises noticeably only at low temperatures. The MnO formed, which has a high melting point (1785°C), yields alloys with FeO and, as is obvious from the state diagram of the FeO-MnO system (see Fig. 18), the melting point of these alloys rises with MnO concentration.

With high concentrations of manganese in the metal, however, solid deoxidation products in the form of mixed crystals begin to segregate already at high temperatures.

When making rimming steels, manganese alone is commonly used as deoxidant since it is unable to reduce the oxygen content of the steel to the 'fully killed' point. The boiling of steel in the mould, even when there is 0.40-0.50 per cent Mn in it, clearly shows that manganese is a less effective deoxidant than carbon.

DEOXIDATION WITH SILICON

The deoxidation reaction with silicon

$$[\mathrm{Si}] + 2[\mathrm{FeO}] \rightleftarrows (\mathrm{SiO_2}) + 2[\mathrm{Fe}]$$

proceeds with the formation of a silicate—fayalite

$$(\mathrm{SiO_2}) + 2(\mathrm{FeO}) \rightleftarrows 2(\mathrm{FeO})\cdot(\mathrm{SiO_2})$$

Another silicate, grunerite $\mathrm{FeO\cdot SiO_2}$, can probably exist in the molten slag, too. The formation of fusible silicates favours the removal of oxygen from the metal.

In the conditions of the acid process, i.e., when the slag is saturated with $\mathrm{SiO_2}$, the concentration of this oxide may be taken as constant in the expression for the equilibrium constant of the deoxidation reaction $[\mathrm{Si}] + 2[\mathrm{FeO}] \rightleftarrows (\mathrm{SiO_2}) + 2[\mathrm{Fe}]$, i.e.

$$K_{\mathrm{Si}} = \frac{(\mathrm{SiO_2})}{[\mathrm{Si}]\cdot[\mathrm{FeO}]^2} = \frac{\mathrm{const}}{[\mathrm{Si}]\cdot[\mathrm{FeO}]^2}$$

or

$$K_{\mathrm{Si}} = [\mathrm{Si}]\cdot[\mathrm{FeO}]^2$$

or else

$$K_{\mathrm{Si}} = [\mathrm{Si}]\cdot[\mathrm{O}]^2$$

The low content of oxygen in steels at equilibrium presents difficulties in quantitative determinations, so that discrepancies are observed between the values of K_{Si} in the published results: 0.17×10^{-4}; 1.49×10^{-4}; 0.56×10^{-4}; 7.1×10^{-4}.

In certain cases another expression for the reaction constant

$$K_{\mathrm{Si}} = [\%\ \mathrm{Si}]\cdot[\%\ \mathrm{O}]^2$$

proves more convenient; for a temperature of 1600°C, it gives $K_{\mathrm{Si}} = 3.6 \times 10^{-5}$.

According to Schenck, the analytical dependence of K_{Si} on absolute temperature is

$$\log K_{\mathrm{Si}} = \log [\mathrm{FeO}]^2 [\mathrm{Si}] = -\frac{32{,}800}{T} + 14.25$$

In the basic open-hearth process, silicon is observed to have a strong deoxidizing effect since free SiO_2 is almost absent in the slag.

For the reaction

$$Si_l + 2O_g \rightleftarrows SiO_2$$

its thermal effect calculated for room temperature ($\Delta H = -207,300$ cal at 25°C) is corrected for 1600°C by the Kirchhoff formula, which gives: $\Delta H_{1,600} = -214,300$ cal.

Considering further that the heat evolved through dissolution of Si_l in iron is 29,000 cal per gram-atom of the silicon added in liquid state and that the heat of dissolution of oxygen is 66,120 cal per mole O_2 [since $^1/_2O_2$ (gas) $=$ O (liquid); $\Delta F^0 = -33,060 + 2.04T$], the thermal effect of the reaction above is found to be

$$\Delta H = -214,300 + 29,000 + 66,120 = -119,180 \text{ cal}$$

Substituting the value of the constant $K_{Si} = 3.6 \times 10^{-5}$ for 1600°C found experimentally into the expression for the free energy of the reaction, we get

$$\Delta F^{\circ} = 4.575 \log (3.6 \times 10^{-5}) = -38,100 \text{ cal}$$

Then substituting the values of ΔF^0 and ΔH obtained in the equation

$$\Delta F^{\circ} = \Delta H - T\Delta S$$

the change of enthropy is found as

$$\Delta S = -\frac{81,080}{T} = -43.5$$

The free energy of the reaction $SiO_2 = Si + 2O$ is then expressed by the equation

$$\Delta F^{\circ} = -119,180 \quad 43.5T$$

whence the equilibrium constant is obtained as

$$\log K_{Si} = -\frac{26,050}{T} + 9.5$$

Calculating the equilibrium constant by this formula gives

Temperature, °C	1540	1590	1650	1700
$K_{Si} = [\% \, Si] [\% \, O]^2$	1.2×10^{-5}	3.2×10^{-5}	9.1×10^{-5}	2.0×10^{-4}

Quantitative relationships between the silicon and oxygen coexisting at equilibrium are shown graphically in Fig. 130.

The relationships found earlier for pure SiO_2 are also applicable for equilibrium with slags saturated with silicic acid, i.e., for acid slags.

In basic slags, silica combines with basic oxides CaO, MgO, and MnO, so that its activity is negligible, with the result that deoxidation with silicon proceeds deeper in the basic process than in the acid process.

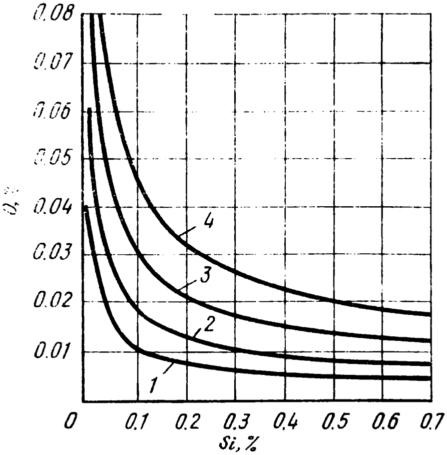

Fig. 130. Isotherms of equilibrium constants for silicon and oxygen
1—at 1540°C; *2*—at 1590°C; *3*—at 1650°C; *4*—at 1700°C

As can be seen from Fig. 130, silicon is a strong deoxidant. With 0.2 per cent of residual silicon in steel, the amount of oxygen in equilibrium with it is only 0.007 per cent (at $t = 1540°C$). But silicon must not be used alone for steel deoxidation, since the products of deoxidation are solid particles uncapable of coalescing. It is advisable to use silicon in combination with manganese, and still better with silico-manganese which forms liquid products of deoxidation.

DEOXIDATION WITH ALUMINIUM

Aluminium is the most effective of the deoxidants commonly employed in steelmaking. Because of the small amounts of residual oxygen and aluminium in steels, the values of the quilibrium constant of the deoxidation reaction with aluminium found experimentally are rather divergent, as will be shown later.

For the reaction of deoxidation with aluminium

$$[3FeO] + [2Al] = [3Fe] + [Al_2O_3]$$

its equilibrium constant is

$$K'_{Al} = \frac{[FeO]^3 \cdot [Al]^2}{[Al_2O_3]\,[Fe]^3}$$

Assuming the concentrations of [Fe] and $[Al_2O_3]$ in the metallic bath to be constant, the equilibrium constant can be written in a simpler form

$$K_{Al} = [Al]^2\,[FeO]^3$$

For a temperature of 1600°C this constant found experimentally is

$$K_{Al} = 5.1 \times 10^{-7}$$

The equilibrium relationships between aluminium and the oxygen dissolved in liquid iron are shown in Fig. 131. Of the three deoxidants, Mn, Si, and Al most often used in steel-making, aluminium is the strongest. For instance, the residual concentrations of oxygen in steel in equilibrium with 0.1 per cent of manganese, silicon or aluminium are respectively 0.175, 0.021, and 0.00028 per cent at 1600°C and 0.12, 0.009, and 0.00013 per cent at 1500°C. But aluminium should not be used alone for obtaining extremely low concentrations of dissolved oxygen, since this may cause the formation of solid alumina, if the reaction

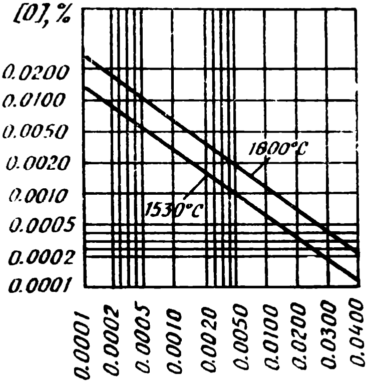

Fig. 131. Diagrams of equilibrium between aluminium and oxygen dissolved in molten iron

$$2[Al] + 4[O] + Fe_l = (FeO \cdot Al_2O_3)$$

has not enough time to proceed.

DEOXIDATION WITH VANADIUM

Vanadium is a very weak deoxidant. It is inferior in its deoxidizing ability to silicon, but still stronger than manganese. For that reason, vanadium is used in small lots for ladle additions to control the intensity of metal boiling in moulds and to improve the grain size when making rimming steels for stamping.

Deoxidation of steel with vanadium follows the reaction $2\,[V] + 4\,[O] + [Fe] = (V_2O_3 \cdot FeO)$, the products of deoxidation being vanadium spinel V_2O_3 and ferrous oxide FeO. The equilibrium of the reaction can be expressed by the equation

$$\log K_V = \log \frac{1}{[\%\ V]^2 [\%\ O]^4} = \frac{42{,}000}{T} - 15.88$$

DEOXIDATION WITH TITANIUM

Titanium, which is an analogue of silicon, is also employed for deoxidation and alloying, usually as a ferro-alloy (see Table 35). The reactions of deoxidation with titanium are

$$Ti + 2[O] = TiO_{2_s}$$

$$Ti + 4[O] + 2[Fe] = Fe_2TiO_{4_l}$$

The precise values of the equilibrium constants for deoxidation with titanium are still unclear. For the former reaction, the equilibrium constant at 1600°C is

$$K_{Ti} = [\%Ti] \cdot [O]^2 = 3.31 \times 10^{-6}$$

Titanium is a very strong deoxidant. With 0.05 per cent Ti contained in steel, the equilibrium oxygen at 1600°C does not exceed 0.004 per cent. Deoxidation with ferro-titanium is made in the ladle, after adding ferro-manganese and ferro-silicon. Under these conditions of deoxidation, medium carbon steels are found to have no free inclusions of titanium oxides, since they are combined into complex silicates. When steel is deoxidized with ferro-titanium alone (up to 0.05 per cent Ti), liquid inclusions of the type of titanium-magnetite spinel $2FeO \cdot TiO_2$ are formed, and at higher concentrations of titanium (up to 0.5 per cent), solid inclusions TiO_2. Thus, at concentrations up to 0.05 per cent, titanium is preferable over aluminium as it gives liquid deoxidation products.

DEOXIDATION WITH ZIRCONIUM

Zirconium, like titanium, is an analogue of silicon. The free energy of the reaction of deoxidation with zirconium

$$[Zr]+2[O]=ZrO_{2_s}$$

can be calculated by the formula

$$\Delta F^{\circ}=-234{,}360+35.6T$$

Apart from being a powerful deoxidant, zirconium has a favourable effect on desulphurization and removal of nitrogen from steel. The reaction of formation of zirconium nitrides

$$Zr_s+1/2N_2=ZrN_s$$

is exothermic, its free energy being expressed as

$$\Delta F^{\circ}=-82{,}000+22.0\,T$$

Zirconium is one of the strongest deoxidants. The products of its deoxidation (ZrO_2) are very high-melting, which explains the fact why the amount of these products passed from metal to slag is insignificant. Along with ZrO_2, zirconium silicates and nitrides may be formed. Small amounts of zirconium are sometimes added to steel to increase its corrosion resistance, wear resistance and ductility.

DEOXIDATION WITH BORON

Among the novel deoxidants, boron will probably prove important. Thermodynamic calculations indicate that boron is a stronger deoxidant than silicon, but inferior to aluminium, though reliable experimental data on its deoxidizing effect are still absent. Its deoxidation reaction can be written as

$$2[B]+3[O]=B_2O_{3_l}$$

In its oxidizing ability, boron exceeds silicon and vanadium and is close to zirconium and aluminium in its effect, which is in full agreement with its place in Mendeleev's Periodic Table. When steel is to be alloyed with boron, it must first be deoxidized with zirconium, aluminium, and calcium. If boron is introduced as a complex alloy containing also aluminium or calcium, these elements reliably protect boron against oxidation, provided that their concentration is sufficiently high. Examples of boron-containing alloys are FeB which contains 11 per cent B, and grainal containing 10 per cent Al, 15 per cent Ti, 3 per cent Si, 25 per cent V, and 0.25 per cent B.

To increase the hardenability of steels, boron is introduced in such an amount as to give a residual content between 0.001 and 0.005 per cent.

Boron forms a solid substitutional solution in the crystal lattice of α-Fe and an interstitial solution in γ-Fe, though, according to other data, it forms solid interstitial solutions in both cases.

DEOXIDATION WITH CALCIUM

At the temperature of liquid steel, calcium can exist only in gaseous state (its boiling point being 1487°C), so that the reaction of deoxidation with calcium is written as

$$\{Ca\} + [O] = CaO_s$$

Its deoxidizing ability is found by the equation

$$\log K_{Ca} = \log \frac{1}{p_{Ca}\,[\%\ O]} = \frac{35{,}900}{T} - 10.9$$

Calcium is a very powerful deoxidant. A very low concentration of oxygen dissolved in metal can be ensured even with a relatively low partial pressure of calcium vapours. For instance, at $p_{Ca} = 0.001$ at and 1600°C, the equilibrium content of oxygen in the metal is 5.6×10^{-6} per cent.

In practical conditions, however, calcium cannot be retained in the metal, whether in furnace or ladle. For that reason, calcium cannot be used for direct reduction of the oxygen content of the metal.

Its role is, however, important if calcium is used in combination with other elements for deoxidation of steel. In that case the products of deoxidation contain a certain amount of CaO, which is sufficient to increase the deoxidizing ability of the accompanying elements by activizing their oxides in the reaction products.

Besides, when present in the deoxidation products, CaO affects their state of aggregation by favouring the formation of fusible compounds which are easily removed with slag. As has been established, globular inclusions are formed in the presence of CaO; this is indicative of the fact that the deoxidation with calcium gives liquid products.

As has been found from the analysis of non-metallic inclusions and the degree of contamination of steels, deoxidation of steel with a silicon-manganese-calcium alloy (69.9 per cent Si, 13 per cent Mn, and 15.5 per cent Ca) produces large globular inclusions, their quantity being not high.

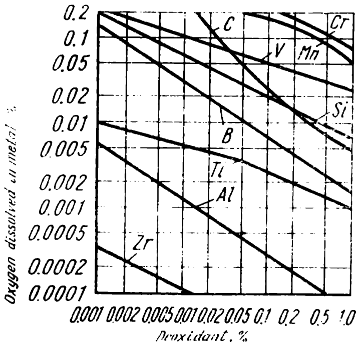

Fig. 132. Deoxidizing ability of certain elements at 1600°C and atmospheric pressure

Some researchers recommend the use of silico-calcium (60 per cent Si and 28 per cent Ca) as a deoxidant, which, for instance, is claimed to improve the quality of tyre steels as regards their content of non-metallic inclusions.

Figure 132 shows a graph of the variations in the deoxidizing ability of certain elements at 1600°C and atmospheric pressure with the varying amount of oxygen in equilibrium with the deoxidant on condition that the activity of the resultant oxides is unity. It is clear that zirconium has the highest deoxidizing ability among the elements being compared. Carbon is seen to have a lower deoxidizing ability than silicon at its concentrations of up to 0.16 per cent and a higher ability at higher concentrations (the curves for Ca and Si intersect).

COMPLEX DEOXIDANTS

As we already know, the metallic bath upon precipitation deoxidation becomes temporarily contaminated with non-metallic inclusions.

The most commonly used deoxidant—manganese (the melting point of its oxide being 1785°C)—combines with the residual FeO to form a continuous series of solid solutions which mostly have their melting points within the range of steelmaking temperatures and are therefore capable of coagulating and coalescing.

As follows from the equilibrium diagram in Fig. 133, when steel is deoxidized with silicon alone (its oxide SiO_2 having the melting point of 1713°C), fayalite $2FeO \cdot SiO_2$ with a congruent melting point at 1205°C, and two eutectics that melt at 1177° and 1178°C, are formed only in a narrow sector of the diagram. Experience shows that special measures must be taken when employing this deoxidant to avoid inordinate contamination of the steel.

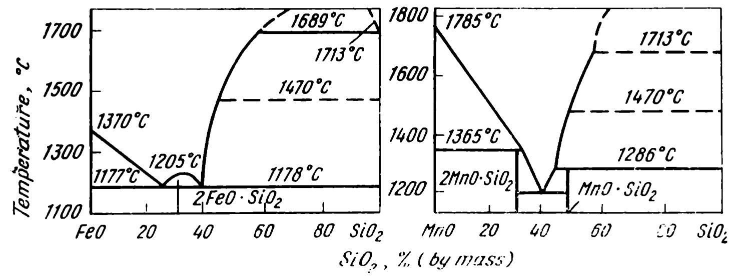

Fig. 133. Phase diagrams of FeO-SiO_2 and MnO-SiO_2 systems

Even greater care is needed when using aluminium, as its oxide melts at 2050°C and is unable to coagulate and probably to float up in the steel because of the needlelike shape of its crystals.

When complex deoxidants are employed, both acid and basic oxides are formed simultaneously in such concentrations that their resultant alloy has a sufficiently low melting point and therefore it remains liquid for a long time. The finely dispersed liquid spheroids have thus enough time to coalesce and rise through the metal to the slag.

The simplest type of such alloys are two-component alloys of silicon and manganese (silico-manganese, silico-spiegel). The equilibrium diagrams of the FeO-SiO_2 and MnO-SiO_2

systems given in Fig. 133 show that fusible manganese and iron silicates can be formed in many FeO-MnO-SiO_2 alloys.

The AMS alloy consisting of 10-30 per cent Mn, 10-20 per cent Si, and 6-20 per cent Al, is widely employed for deoxidation.

In the absence of complex deoxidizing alloys, it is recommended to follow a certain order in adding separate deoxidants. Thus, the addition of manganese prior to silicon promotes the formation of fusible silicates since liquid alloys of the (Mn, Fe)O type begin to form before the precipitation of silica.

Experience shows that binary and ternary complex deoxidants (Si-Mn, Si-Ca, Ca-Al, Al-Mn-Si, Al-Si-Ca) forming fusible compounds capable of coalescing and floating up in the metal, reduce by half the amount of non-metallic inclusions in steels.

Fusible inclusions which can be easily removed from the metal are formed when a silico-manganese ferro-alloy with the Mn/Si ratio of from 5 to 7 is used for deoxidation. With this ratio of the components in the alloy, the products of deoxidation are not saturated with silica and remain liquid in the metal. The oxide formed through deoxidation is never rich in silica, since it is fluxed by manganous oxide; this inevitably causes the formation of liquid silicates.

In addition, the deoxidizing effect of each deoxidant is reinforced when several deoxidants are employed simultaneously. For instance, it has been established experimentally that the deoxidizing ability of silicon is much improved by the presence of manganese. The same is true of aluminium. The mechanism of enhancing the effect of strong deoxidants in the presence of a weak one has not yet been properly explained. It is believed that it is caused by some interplay of the activities of the deoxidant and the oxygen in the metal, and also by the reduction in the activity of each of the resultant oxides in the reaction zone owing to the processes of neutralization of acid oxides by basic ones.

Figure 134 shows how the deoxidizing ability of certain elements is improved when a weak deoxidant is simultaneously present in the melt. Even the deoxidizing ability of aluminium is increased in the presence of another deoxidant.

Consequently, from the standpoints of obtaining more fusible deoxidation products and of increasing their deoxidizing ability, simultaneous deoxidation with silicon and manganese is preferable to their separate application. It is therefore more beneficial to use a complex ferro-alloy, e.g. silico-manganese, and not silicon and manganese in the form of separate ferro-alloys. Separate, even simultaneous, introduction of silicon and manganese ferro-alloys into the bath may cause partial formation of high-silica deoxidation products in certain parts of the bath in the form of solid silica or manganous oxide; the silica then undoubtedly reacts with the manganous oxide and ferrous oxide but very slowly, and as a result the steel becomes contaminated with fine silica crystals.

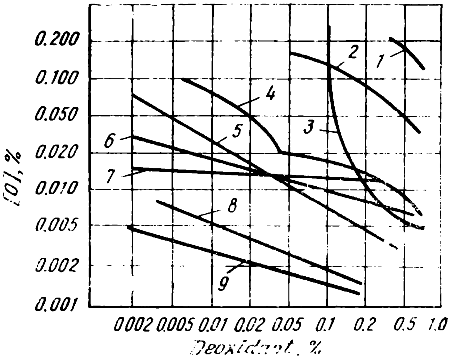

Fig. 134. Deoxidizing ability of certain elements in combined action
1—Cr; 2—Mn; 3—C; 4—Si; 5—Al; 6—Si+0.5% Mn; 7—Si + 0.25% Mn; 8—Al + 0.5% Mn; 9—Al + 0.66% Mn + 0.27% Si

When steel is deoxidized first with manganese and then with silicon, or vice versa, the second deoxidant will react with the oxygen dissolved in the metal in the presence of the resultant deoxidation products of the first deoxidant. These products are very high-melting and inactive and therefore cannot change rapidly the composition of the slag phase in the reaction zone.

When complex deoxidants are employed, the deoxidation products are usually liquid, which facilitates their coalescence, aggregation, and comparatively rapid removal from metal to slag.

For the processes of coalescence and coagulation of nonmetallic inclusions to proceed successfully, particles of inclusions must get free of the liquid metal, i.e., they have to perform some work to overcome their sticking to the metal (the work of adhesion). As is known, the work of adhesion decreases with an increase of the interface tension at the liquid metal-inclusion boundaries. The conditions for coalescence of particles therefore improve when the interface tension between the liquid metal and inclusions is increased.

An elevated temperature and a lower viscosity of the melt are favourable in accelerating the floating up of inclusions. One has to keep in mind that high concentrations of chromium, tungsten, molybdenum and titanium in the melt increase its viscosity and therefore the heat must be finished at an elevated temperature. On the contrary, a higher content of carbon, manganese, silicon, calcium or copper reduces the viscosity of the melt.

We have considered the conditions for combined deoxidation of steel with two or three deoxidants and established that the activity of each of the oxides formed reduces when the products of deoxidation are in the same phase and subjected to full or partial fluxing. As a result, the element whose oxide has been fluxed acquires a higher deoxidizing ability. The following rule may be used in such cases: if the deoxidation products enter the composition of the liquid oxide phase, for instance, $(MnO)_n \cdot (SiO_2)_n$, the deoxidizing ability of each of the deoxidants will be greater than in the case when the products of deoxidation are solid phases of pure oxides, for instance, SiO_2 and MnO.

Let us now discuss the case of simultaneous deoxidation of steel with two deoxidants under the conditions that the products of deoxidation are in different phases, for instance, the products of deoxidation formed by one of the deoxidants are in the gaseous phase, and those formed by the other, in an inactive condensed phase in the form of slag particles. In such cases the residual content of oxygen in the steel is governed by the deoxidizing ability of the stronger deoxidant.

Let the deoxidation be carried out simultaneously with silicon and carbon. We assume that upon addition of the deoxidants the bath contains 0.2 per cent C and 0.1 per cent Si. Then, as can be seen from Fig. 132, 0.015 per cent O_2 can be in equilibrium with carbon and 0.020 per cent O_2 with silicon at a temperature of 1600°C. It is then natural that the carbon will be the principal deoxidant under the given conditions and that the product of deoxidation will be CO. The silicon will then acquire only an insignificant number of atoms of dissolved oxygen in local zones near lumps of ferro-silicon where the concentration of silicon during dissolution is high, but in general the silicon will not participate in the deoxidation reaction. Therefore, under these conditions of deoxidation with two elements, none of them acquires a higher deoxidizing ability.

If we change the ratio of their concentrations by increasing the content of silicon up to 0.3 per cent, then only 0.01 per cent oxygen will remain in equilibrium with silicon, which exceeds the deoxidizing ability of the carbon. In that case silicon will be the main deoxidant; no carbon oxide will be formed since the carbon cannot participate in the process of deoxidation (because the silicon picks up all the oxygen dissolved).

Finally, when the silicon content is made equal to 0.2 per cent, its deoxidizing ability will be the same as that of carbon. They both will participate in the deoxidation process, but the residual content of oxygen in the metal will depend on the deoxidizing ability of each of the elements, since they do not enhance each other's deoxidizing ability because their products of deoxidation are in different phases.

The modern trend is to deoxidize steel in the ladle rather than in the furnace. This method makes it possible to increase the productivity of furnaces and, in addition, permits easy removal of the products of deoxidation formed upon addition of ferro-alloys and alloying elements from the metal into the slag phase owing to powerful currents in the ladle caused by the jet of tapped metal.

The experimental curves in Fig. 135 clearly show that the total content of oxygen in steel (i.e., dissolved oxygen plus oxide inclusions) reduces sharply just during tapping and teeming. When, however, the metal is kept in the ladle for a certain time, the total content of oxygen, including the oxygen in high-melting inclusions Al_2O_3, ZrO_2, and TiO_2, drops only insignificantly.

Extensive laboratory and industrial studies are required before aluminium can be recommended for use in large

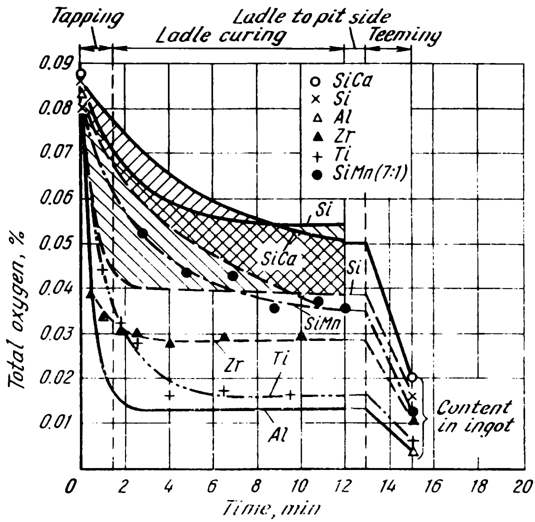

Fig. 135. Variations of the total oxygen content of steel during tapping, ladle curing and teeming (after E. Plöckinger)

amounts for deoxidation, since, as is well known, it forms very fine, solid, high-melting, and sharp-edged inclusions in the metal. It should be remembered that small additions of aluminium cause the formation of $FeO \cdot Al_2O_3$, while Al_2O_3 is predominantly formed when aluminium is given in large amounts.

DIFFUSION DEOXIDATION

Diffusion deoxidation, which is based on the law of distribution of ferrous oxide between the metal and slag, comes essentially to deoxidation of the slag. Lowering the concentration of FeO in the slag causes the oxygen to diffuse from the metal to slag until an equilibrium is established between the two phases at a given temperature:

$$(FeO) + [Me] \rightleftarrows (MeO) + [Fe]$$

$$[FeO] \rightleftarrows (FeO)$$

When FeO of the slag is deoxidized with aluminium, silicon or carbon, reversion of phosphorus from slag to metal is inevitable. For that reason the initial slag must be removed as completely as possible from the furnace and a new slag formed by adding lime, fluorspar and bauxites.

Reduction of iron oxides in the slag is effected in practice by spreading powdered deoxidizing mixtures in several steps onto the surface of the slag in the furnace. The gaseous atmosphere in the furnace should then be kept as little oxidizing as possible in order to minimize the loss of the elements in the deoxidizing mixture.

An essential advantage of diffusion deoxidation is that the metal becomes comparatively free of non-metallic inclusions. Practical examples of diffusion deoxidation are given below.

Deoxidation with a mixture of aluminium powder and burnt lime (60-65 per cent Al and 40-35 per cent CaO). The mixture is added in an amount of 3 per cent of the mass of metal. The method requires some measures to be observed.

The slag must not be strongly oxidizing at the moment of adding the mixture, nor should it be excessively basic (not above 3.0) so as to avoid 'secondary oxidation' of the metal through decomposition of calcium ferrites which are characteristic of this type of slag.

The skimming of the dephosphorizing slag and adjusting of new slag must be done at the end of the refining period by gradually introducing a deoxidizing mixture consisting of ferro-silicon, ground coke, and lime; only the final deoxidation is to be carried out with powdered aluminium and burnt lime. While deoxidizing mixtures are being introduced, a high positive pressure and a smoky flame must be formed in the furnace (by closing the valves).

Another method consists in that three types of mixture—slag-forming, reducing, and deoxidizing—are successively introduced into the furnace after slagging-off. The percentage composition of the mixtures is as follows:

I. *Slag-forming mixture:*

lime	86.0
moulding sand	14.0
	100.0

II. *Reducing mixture* (AMS alloy being preliminarily added in an amount of 0.27 per cent of mass of metal):

CaO	48.5
Ca	16.1
Coke	16.1
charcoal	16.1
moulding sand	3.2
	100.0

III. *Deoxidizing mixture:*

75- or 90-% ferro-silicon	66.6
charcoal	33.4
	100.0

In mixtures II and III, charcoal is sometimes replaced by coke, and ground fireclay is added to mixture II. Deoxidation by this method reduces the contents of FeO and MnO in the slag respectively from 9.0 to 1.5 per cent and from 5.0 to 1.6 per cent. The slag becomes grey.

Still another method of diffusion deoxidation is worth mentioning. First, 0.5 per cent Si is added into the metal for preliminary deoxidation, and then calcium carbide CaC_2 and aluminium are added to the slag. The method may be regarded as a combined one since diffusion deoxidation is combined here with precipitation deoxidation.

Owing to an extended period of diffusion deoxidation and consequently the reduction of furnace productivity, and also a high cost of the deoxidants used in the process, this method proves efficient only for making high-quality alloy steels, since chromium and manganese can then be reduced from the slag.

DEOXIDATION WITH SYNTHETIC SLAGS

In this method, the surface of contact between the metal and slag is increased whenever possible to a maximum by pouring the metal from a considerable height (up to six metres) and at a great speed into a ladle containing synthetic slag. The passage of FeO from metal to slag, $[FeO] \rightarrow (FeO)$, which is slow in the normal conditions of diffusion deoxidation, is then accelerated due to an intensive mixing of the molten metal with the slag.

This method enables not only the extraction of ferrous oxide from the metal by the slag, but also the reduction of the elements from the oxides of the emulsified slag in the ladle, since the large speed of metal pouring increases the contact surface between the metal and the emulsified slag many times, up to 100 m^2 per m^3 of metal.

Both methods, i.e., diffusion deoxidation and treatment with synthetic slags, are identical in their physico-chemical principles, but differ substantially in their practical realization. The first method requires much time to treat the slag in the furnace, while the second is very rapid because of the intensive emulsification of the slag in the metal. Acid slags are used for treating basic metal and basic slags, for acid metal.

Basic slags with a very low content of $\Sigma(FeO + MnO)$, obtained in electric furnaces, are also utilized for deoxidation; their composition may be as follows: 65 per cent CaO, 13 per cent SiO_2, 2 per cent Al_2O_3, 15 per cent CaF_2, 4 per cent MgO, 1 per cent FeO, 0.20 per cent MnO, 0.10 per cent P_2O_5, and up to 1 per cent CaC_2. Such slags have both a desulphurizing and a deoxidizing action. The use of these highly basic slags to treat acid steel greatly reduces the contamination of the steel with finely-dispersed, siliceous slime; the treatment of the killed basic steel by these slags gives a reduction of the total content of inclusions.

Open-hearth steels treated with a synthetic slag of proper composition are not inferior in their properties to electric steels. By using this method, it is possible to control the mineral composition of residual non-metallic inclusions and their amount in steels.

Experiments indicate, for example, that by its properties the basic steel treated with acid synthetic slags resembles the steel made by the acid process, namely that the difference in the mechanical properties of forged or rolled metal in both longitudinal and transverse directions (anisotropy) is largely smoothed out. On the other hand, treating the acid steel with a basic-type slag reduces its tendency to crack through sharp temperature changes when it is heated for hot mechanical working.

There is a view that the mixing ladle should be replaced by a more advanced apparatus to provide quicker mixing of the molten metal and slag, for instance, by a ladle rotating around its vertical axis, a ladle in which the metal is stirred under the action of an a.c. source, or a rotatable tubular runner in which the metal is mixed with the liquid slag or solid powder.

COMBINED METHOD OF DEOXIDATION

A new method of deoxidation has been introduced into practice, which combines diffusion deoxidation and slag treatment during melting in a tilting open-hearth furnace. The metal is tapped through a greatly enlarged taphole together with the slag that has been deoxidized in the furnace. Vigorous agitation of the metal and the slag in the ladle leads to further desulphurization and removal of slag inclusions.

As stated earlier in the book, the method of treating open-hearth, converter and electric steels with fluid limy high-alumina slags containing 52-53 per cent CaO, 44-45 per cent Al_2O_3, and 1.0-1.2 per cent SiO_2 has been successfully employed for the removal of sulphur and non-metallic inclusions. Irrespective of the type of steel and its initial sulphur content (0.04-0.15 per cent), the amount of sulphur drops after slag treatment to about 0.006 per cent in high-carbon steels and to 0.012 per cent in low-carbon steels with the simultaneous reduction of non-metallic inclusions and oxygen content. The method finds application mainly for making critical grades of steel.

VACUUM REFINING OF STEEL

In modern practice, vacuum refining of steel outside the furnace is made in ladles or other vessels, with the metal being sometimes circulated. The method is based on the fact that the deoxidizing ability of the carbon dissolved in liquid metal increases many times in vacuum. This is because the product of the reaction of deoxidation, $C + O \rightarrow CO$, is continuously drawn off from the vacuum chamber with the result that the reaction proceeds vigorously to the right. Even at a residual pressure of 1 mm Hg in the chamber, the deoxidizing ability of carbon exceeds that of aluminium (see Fig. 132).

Critical grades of steel in which the residual contents of hydrogen and oxygen and non-metallic oxide inclusions must be as low as possible are subjected to vacuum refining prior to adding strong deoxidants, such as silicon; this provides conditions for the reactions of self-deoxidation of the carbon and oxygen dissolved in the metal to proceed effectively. The treatment takes from 8 to 10 minutes, which is sufficient to reduce substantially the concentration of the dissolved oxygen. Then, to bring the steel to the specification, ferro-alloys and alloying additives (FeSi, FeCr, Al, etc.) are charged into the metal from bunkers installed in the vacuum chambers and provided with vacuum gates, after which the vacuum treatment is continued for another 2 to 4 minutes to remove the gases brought in with the ferro-alloys and to distribute the latter uniformly in the metal.

This method of deoxidation makes it possible to save deoxidants and alloying additives, since the principal deoxidizing effect is provided by the carbon dissolved in the metal. After the vacuum treatment the metal is cast into moulds or is delivered to continuous casting plants where the metal jet is protected by argon.

2. ALLOYING OF STEEL

Concurrent with the process of deoxidation, the metal is brought to the specified analysis. The steel is termed alloyed if the content of alloying elements in it is greater than in common carbon steel. For instance, a steel is related to the category of alloy steels if it contains more than 0.6 per cent Si or more than 0.8 per cent Mn, while common carbon steel usually contains 0.17-0.37 per cent silicon and not more than 0.7 per cent manganese.

Various alloying elements are employed in steelmaking, whose presence imparts special mechanical and other properties to the steel. These may be either metals (Mn, Ni, Co, Cu, etc.) or non-metals (C, S, P, N). Their solubility in iron may be very diverse, some elements (Pb, Ag, Bi) being practically insoluble.

Thus, alloy steels are alloys of iron, carbon, and some alloying elements which ensure special properties. Alloy steels may be classed into the following groups according to the number of alloying components:

1. Simple (ternary) alloy steels, i.e., those containing a single alloying element in addition to iron and carbon. The steel is named after the alloying element, for instance, chromium steel, nickel steel, etc.
2. Quaternary alloy steels, i.e., those containing two alloying elements, apart from iron and carbon (for instance, chrome-nickel steel, chrome-molybdenum steel).
3. Complex alloy steels containing more than two alloying elements.

The properties of steels (strength, ductility, corrosion resistance, scale resistance, wear resistance, magnetic properties, etc.) may be controlled within wide ranges by properly selecting their composition. An unfavourable effect of an element may be partially compensated for by introducing another element.

Silicon, manganese and chromium are less deficient and cheaper alloying elements, while vanadium, tungsten, cobalt, molybdenum and some other elements are more expensive. A steel should be given desired properties whenever possible by using less expensive elements in its composition, subsequent heat treatment being helpful in some cases.

Alloy steels produced in the USSR are designated by Russian letters and numerals (Table 51), the letters denoting the alloying element. Numerals before the letters designate the average content of carbon in tenths (one digit) or hundredths (two digits) of a per cent. Numerals after the letters denote the approximate content of the alloying element in

Table 51

Designation of Elements in Alloy Steels

Element	Chemical symbol	Russian symbol	Element	Chemical symbol	Russian symbol
Manganese	Mn	Г	Cobalt	Co	К
Silicon	Si	С	Aluminium	Al	Ю
Chromium	Cr	Х	Copper	Cu	Д
Nickel	Ni	Н	Boron	B	Р
Tungsten	W	В	Niobium	Nb	Б
Vanadium	V	Ф	Zirconium	Zr	Ц
Titanium	Ti	Т	Phosphorus	P	П
Molybdenum	Mo	М	Nitrogen	N	А

integral percentage numbers; if the steel contains less than 1.5 per cent of an element, no digit is written after the letter.

For instance, the designation 60С2 implies that the steel contains 0.55-0.65 per cent C and 1.8-2.0 per cent Si; 40Х is a steel containing 0.35-0.45 per cent C and 0.8-1.1 per cent Cr; 7Х3, a steel containing 0.60-0.75 per cent C and 3.2-3.8 per cent Cr, etc.

High-quality steels very fine from sulphur and phosphorus are denoted by the Russian letter А put at the end of the notation. For example, steel 12Х2Н4А is a high-quality steel containing 0.12 per cent C, roughly 2 per cent Cr, and around 4 per cent Ni.

Some grades of steel are designated by the letters characterizing their group or type with the addition of a digit (or a letter and digit) to indicate the approximate content of carbon or an alloying element. The following designations are in use in the USSR: У—carbon tool steel, for instance, У7 (0.65-0.74 per cent C); А—free-cutting steel, for instance, А20 (0.15-0.25 per cent C); Р—high-speed steel, for instance, Р18 (17.5-19.0 per cent W); Ш—ball bearing steel, for instance, ШХ15 (1.3-1.6 per cent Cr); Е—magnet steel, for instance, ЕХ3 (2.8-3.6 per cent Cr); Э—electrical steel, for instance, Э11 (0.8-1.8 per cent Si). Open-hearth steels are denoted by the letter М; Bessemer steels, by Б; basic Bessemer steels, by Т; and oxygen-converter steels, by К.

The melting of an alloy steel differs from that of a common quality carbon steel only in that some alloying elements are added to the metal (most often as ferro-alloys). The elements: manganese, silicon, chromium, nickel, molybdenum, and tungsten are predominantly used for alloying.

MODIFICATION AND MICROALLOYING OF STEELS

Modification is the refinement of the grains of the initial crystalline structure of steel by introducing into the melt a small amount of elements or their compounds which are termed modifiers.

Modifiers of the first kind are surface-active metals almost insoluble in the melt; they are absorbed at the crystal-melt boundaries. These modifiers envelop the surface of tiny crystals and retard their growth, thus ensuring fine-crystalline structure of cast steel.

Modifiers of the second kind are very high-melting metals and their oxides, nitrides and carbides, which are added into the melt in small amounts in order to form a large number of crystallization centres and thus provide a fine-crystalline structure for cast steel. It is desirable to use modifiers obeying the principle of orientational and dimensional correspondence, i.e., the modifiers whose crystal lattice differs as little as possible from that of the solidifying phase. Modifiers of this kind must remain solid by the moment of the beginning of solidification of the melt, because only then can they serve as crystallization centres. Modifiers of the second kind often give the same effect as with microalloying. The effects provided by modifiers of both kinds can also be obtained by ultrasonic treatment of the melt.

Microalloying of steel. This term still has no general interpretation. Microalloying is understood here as introducing 'small additions' of elements or their compounds (in amounts not more than 0.1 per cent) into the melt with the aim of improving appreciably the mechanical and service properties of final steel. The effects provided by microalloying are deeper deoxidation, desulphurization and degassing of steel; changes in the shape and properties of particles of non-metallic inclusions and their distribution in microvolumes of the metal; changes in the composition and state of grain boundaries; refinement of metal grains and control of their growth on heating. Microalloying can also affect the critical points, recrystallization temperature, and hardenability of steel.

As follows from what has been said above, modification of steel is similar in its effect to microalloying only when it results both in refinement of the initial structure of cast steel and in a noticeable improvement of its mechanical and service properties.

As has been found experimentally, microalloying improves substantially the structure of the metal and increases its hardenability, strength and plasticity. For instance, structural steel microalloyed with tellurium acquires fine-grained structure and is less prone to overheating. High-manganese steel type Г13Л microalloyed with titanium has better plasticity and higher wear resistance.

The most promising elements to serve simultaneously as desulphurizing and degassing agents are rare-earth metals, which are used as misch-metal and ferro-cerium. Complex alloys with lanthanum (or other rare-earth metals) are more effective for desulphurization than cerium alloys, but less effective in degassing of the metal.

Preliminarily deoxidized structural chrome-nickel and chrome-nickel-molybdenum steels when alloyed with small additions of rare-earth metals (0.10-0.15 per cent) acquire a better structure, better plasticity at sub-zero temperatures, lower red-shortness, and substantially better plasticity in hot working. Modification of steel grade 40ХЛ with ferro-cerium gives the same effect in improving its properties as microalloying with rare-earth metals. Cases are known, however, when the plastic properties of steel were impaired through the presence of residual cerium in excess of 0.05 per cent; as was established experimentally, this was caused by separation of complex cerium compounds at grain boundaries.

The effect of rare-earth metals lies in combining harmful impurities (oxygen, sulphur, hydrogen, and arsenic) into stable high-melting compounds (sulphides, oxides, intermetallic compounds), which results in an improved quality of steel, especially of its plastic properties. Part of the rare-earth metal compounds are removed with the slag, and the remaining part serves as nucleation centres favourable for refining the initial crystalline structure of the metal.

The ability of rare-earth metals to form sulphides, however, sometimes causes the formation in ingots of characteristic sulphide aggregations in the form of sulphur spots. It has also been established that oxide inclusions of an unfavourable shape can also be formed in certain cases. Rare-earth metals are undoubtedly useful for modification and deoxidation of certain grades of steel, whereas their application for other grades of steel may result in a noticeable redistribution of oxides and sulphides and often causes a higher wastage of metal.

The useful role of cerium as a microalloying element would be higher if we managed to calculate exactly its dosage for various kinds of steel at a given teeming temperature in order to form stable complex sulphides, nitrides and hydrides. The amount of cerium to be added to steel must be consumed completely for the formation of these complexes. Cerium is a strong surfactant and thus when left free in the metal even in a very small amount it will be concentrated at boundaries of crystals and impair their discontinuity, i.e., will become a harmful impurity.

As is known, boron is only poorly soluble in iron, its solubility being not higher than 0.005 per cent. It forms a stable iron boride FeB. Because of the poor solubility of boron in liquid iron, borides separate from the solidifying melt and act as nucleation centres, like nitrides or carbides, thus making the structure of steel more fine-grained. The method of adding boron to metal is of high importance. Before adding it, the oxygen, nitrogen, and sulphur dissolved in the metal must be combined into stable compounds; otherwise boron, which has a high deoxidizing power, can oxidize into B_2O_3, B_4O_5, B_2O_2, or B_4O_3 or can easily form a nitride BN and sulphides B_4S and B_2S_3.

PRACTICE OF DEOXIDATION AND ALLOYING

Almost all deoxidizing and alloying elements are added to steel as ferro-alloys and only few of them, in pure form. The main requirement a ferro-alloy should meet is a sufficiently high concentration of the alloying element and possibly low contents of carbon, phosphorus, sulphur, and slag impurities. The need to minimize the loss of ferro-alloys led to the development of the technique of 'preliminary deoxidation', which also lowers the contamination of the final steel by non-metallic conclusions.

Preliminary deoxidation which is employed only in making killed steels is carried out as follows. After the average specified carbon content in the bath has been adjusted, ferro-manganese is introduced, calculated for the lower limit of the manganese content in the final steel, and eight or ten minutes later, blast-furnace ferro-silicon (12 per cent Si) preheated to 600-700°C is added to provide for 0.10-0.17 per cent of silicon in the bath. This order of adding ferro-alloys, or a reverse one, ensures optimum conditions for the coagulation of non-metallic inclusions (as silicates).

When silico-manganese is used for preliminary deoxidation it is introduced into the bath in an amount that will not raise the manganese content of the steel above the upper specified limit. Ten minutes later, while the bath is still not boiling, the final stage of deoxidizing and alloying is started. The technique of introducing ferro-chrome into the boiling bath is now supported by a number of metallurgists. Ferrochrome must be added to the bath in red-hot state. The bath is then cured for 15-30 minutes and agitated several times by rammers to ensure better decomposition of chromium carbides.

The final stage of deoxidation of killed steel consists in introducing additional deoxidants into the jet or ladle during tapping.

In practice, the whole amount of pre-heated deoxidants is sometimes introduced only into the bath, but a combined method is more often employed, by which deoxidation is carried out partly in the furnace and partly in the ladle (or launder). More recently deoxidation of carbon steels, and even of chromium steels, has been carried out simultaneously with alloying in the ladle, exothermic ferro-alloys being often used for the purpose. The loss of ferro-alloys is thus diminished. Light alloys are introduced in a finely ground state either into the jet of steel being tapped or into the ladle, or are added as powder in paper bags (to avoid their loss with dust).

The requisite amounts of metallic aluminium and of bagged carbonizing materials (finely ground graphite, anthracite, or charcoal) are cast into the jet of tapped metal.

Alloying is much facilitated by using elements that are stable against oxidation, as Ni, or Mo. They are completely recovered from the appropriate alloy scrap and are often included into the charge: nickel as pure metal and molybdenum as a ferro-alloy or calcium molybdate. When alloy scrap is used, the content of these elements in the bath is determined after meltdown and any deficiency is made up for. But the elements which are very liable to oxidation (V, Ti) are usually added into the ladle, and then only after ferro-silicon (45- or 75-%) or aluminium have been introduced.

A wide variety of techniques are employed in practice for preliminary deoxidation, although the main conditions of the steelmaking process are strictly specified by standard instructions. Certain grades of steel (Д, Ст. 4, 40Х, etc.) are tapped from the furnace without preliminary deoxidation, since this reduces the loss of silicon from 20-37 per cent to 5-16 per cent and shortens the tap-to-tap times by 15-20 minutes.

In a number of works making killed carbon and alloy steels, the metal is usually first deoxidized in the furnace with manganese and silicon. Some researchers are of the opinion that only by adding silicon to the metal during preliminary deoxidation is it possible to reduce the loss of alloying elements and attain closer control of the carbon content of the steel. This is particularly important, of course, when the carbon content of the steel is specified within very narrow limits. But the disadvantages of the method are a rather high consumption of ferro-alloys, a certain possible, though sometimes hardly noticeable, rise in the hydrogen content of the metal, and an increase in the tap-to-tap time by 5-15 minutes.

When large quantities of ferro-alloys must be added to the ladle for deoxidation and alloying, chilling of the melt is avoided by using exothermic ferro-alloys pressed into briquettes or sometimes packed in tins. Sodium saltpetre $NaNO_3$, potassium chlorate $KClO_3$, and manganese peroxide

MnO_2 are used in briquettes as oxidants; the last two are chosen when it is necessary to prevent the dissolution of nitrogen in the steel as much as possible. The fuels included into exoth rmic ferro-alloys are aluminium, carbon, silicon and silico-calcium.

Briquettes of exothermic ferro-alloys are usually put into the ladle prior to tapping. The absorption of chromium and manganese from them may be as high as 90-95 per cent. It has been found that chromium and manganese are quite uniformly distributed in steel with their contents in it up to 1.6 per cent, provided that briquettes of a thermicity above 420 kcal/kg are used.

The use of exothermic ferro-alloys reduces the tap-to-tap time and thus increases furnace productivity; it also diminishes the consumption of ferro-alloys and fuel. Some experience has been gained in using fluxed exothermic ferro-alloys for deoxidation, alloying, and desulphurization of steel in the ladle. The briquettes generally consist of the required ferro-alloys, a combustible element, an oxidant, and fluxes. The slag formed from the fluxes, the products of exothermic reactions, and the deoxidation products (2.5-3.0 per cent of the mass of the metal) contains approximately 50-55 per cent calcium fluoride, 30-35 per cent alumina, 7-9 per cent sodium oxides, and 8-10 per cent silica, and has a melting point in the range of 1220-1300°C. This slag ensures fluxing of deoxidation products at an early stage of their formation and the content of fluxing elements in the briquettes is sufficient for additional desulphurization of the steel in the ladle when the oxygen concentration after deoxidation is low.

This new technique of deoxidation and alloying in the ladle for steel grades 20X and 40X appreciably decreases the loss of deoxidants: 3.4 per cent Cr, 12.3 per cent Mn, and 15.0 per cent Si (total, including that in the furnace from blast-furnace ferro-silicon and that in the ladle from briquettes). Additional desulphurization in the ladle reaches 36-42 per cent, even though a certain amount of oxidized furnace slag inevitably passes into the ladle. This results not only in deeper desulphurization, but also in better removal of nonmetallic inclusions and therefore in better quality of the steel.

The method for making rimming steel with 0.15-0.22 per cent C deserves attention. The metal decarbonized in the furnace down to 0.08-0.10 per cent C is carbonized in the ladle by adding anthracite or coke. The steel made boils longer and more vigorously in moulds.

The consumption of aluminium is governed by the oxygen content of steel, which is linked with the oxidation of the final slag in the furnace and the carbon content of the bath, and also with the need to form austenitic grains of a definite size in the steel.

In most cases rimming steel is deoxidized with ferro-manganese in the ladle; but it must be always borne in mind that the silicon content of the ferro-manganese must not exceed one per cent, otherwise the metal will not boil well in moulds and the quality of ingots and rolled products will be impaired.

CALCULATION OF FERRO ALLOYS FOR DEOXIDATION

The loss of ferro-alloys is always higher when they are introduced in the furnace than when added to the jet of steel or to the ladle on tapping. The coefficients of the loss of the elements being introduced are found experimentally.

The amount of an element to be added can be calculated by the formula

$$x = \frac{QE\,100}{AP}, \text{ t}$$

where Q = furnace capacity, t

E = element to be introduced, determined as the difference between the specified content and the residual content in the bath, per cent

A = assimilation of the element (100 per cent minus the oxidation loss)

P = content of the alloying element in the ferro-alloy, per cent

Example 1. It is required to make a steel containing 0.80-1.10 per cent chromium. The ferro-chrome available contains 65 per cent Cr. Residual chromium in the bath is taken as 0.10 per cent. Furnace capacity is 100 t.

The average specified content of chromium is (0.80 + + 1.10) : 2 = 0.95 per cent.

Taking into account the residual chromium in the bath, the amount of chromium to be introduced is 0.95 — 0.10 = = 0.85 per cent.

With the oxidation loss of chromium equal to 30 per cent, the consumption of ferro-chrome is

$$x = \frac{100 \times 0.85 \times 100}{70 \times 65} = 1.87 \text{ t}$$

Example 2. It is required to make a rimming steel containing 0.40-0.50 per cent manganese. The ferro-manganese has 70 per cent Mn. Deoxidation is to be made in the furnace, the mass of the metallic bath being 190 t and the content of manganese in it before deoxidation being 0.15 per cent. The loss of manganese in the furnace is expected to be 35 per cent.

The average specified content of manganese in the final steel is (0.4 + 0.5) : 2 = 0.45 per cent. The amount of manganese to be introduced is 0.45 — 0.15 = 0.30 per cent. Then the amount of ferro-manganese to be added to the bath is

$$x = \frac{190 \times 0.3 \times 100}{65 \times 70} = 1.253 \text{ t}$$

Example 3. It is required to make a rimming steel containing 0.40-0.50 per cent manganese. The ferro-manganese contains 70 per cent Mn. Deoxidation is to be made in the ladle. The mass of the metallic bath is 200 t, and the content of manganese in it prior to deoxidation, 0.15 per cent. The loss of manganese in the ladle is expected to be 25 per cent.

The average specified content of manganese in the final steel is (0.4 + 0.5) : 2 = 0.45 per cent. The amount of manganese to be added is 0.45 — 0.15 = 0.30 per cent.

Then the amount of ferro-manganese to be added to the ladle is

$$x = \frac{200 \times 0.3 \times 100}{75 \times 70} = 1.146 \text{ t}$$

Example 4. The mass of liquid metal in the bath is 300 t. Calculate the amount of blast-furnace ferro-silicon containing 12 per cent Si that must be introduced for preliminary de-

Table 52

Recommended Conditions for Introducing Ferro-alloys

Ferro-alloys and alloying additives	Loss, %	Moment of introduction	Lump size of ferro-alloy, mm
Nickel	—	With charge or after meltdown	From shot to 10-12-kg pigs
Ferro-molybdenum	—	As the bath begins to boil	70-80
Ferro-tungsten	30-40	1.5 h before tapping	70-80
Ferro-vanadium	20-30	To ladle on tapping	70-80
Ferro-phosphorus	25-30	Ditto	70-80
Ferro-chrome	15-30	After preliminary deoxidation of the bath	80-100
Ferro-manganese	20-30	5-15 min before tapping or to ladle	80-100
Blast-furnace ferro-silicon	—	To bath	Pigs
High ferro-silicon	15-25	To ladle	15-20 mm, packed in bags
Ferro-titanium	40-50	Ditto	80-100
Sulphur	25-30	Ditto	70-80

Note: The values of loss are approximate and are given only for ferro-alloys introduced after preliminary deoxidation. When rimming steels are deoxidized with ferro-manganese, the loss of the alloy may be as high as 40-50 per cent.

oxidation. Usually 0.15 per cent silicon is added to the bath for the purpose (neglecting the loss of silicon). Then

$$x = \frac{300 \times 0.15}{12} = 3.75 \text{ t}$$

Example 5. The bath contains 300 t of liquid metal. The final steel must have 0.20-0.35 per cent silicon. Calculate the amount of 45-per cent ferro-silicon to be introduced into the launder on tapping, if the ferro-silicon contains 44 per cent Si and its loss is 35 per cent. The average content of silicon in the steel is (0.20 + 0.35) : 2 = 0.28 per cent. The amount of ferro-silicon to be added then is (considering its loss):

$$x = \frac{300 \times 0.28 \times 100}{65 \times 44} = 2.95 \text{ t}$$

Example 6. The last sampling of metal from a 200-ton bath before deoxidation has shown 0.023 per cent phosphorus. Ferro-manganese containing 0.3 per cent phosphorus is added to the ladle in an amount of 1.25 t. Calculate the content of phosphorus in the metal in the ladle.

The ferro-manganese brings in (1250 × 0.3) : 100 = = 3.75 kg phosphorus, which exceeds the phosphorus content in the bath by (3.75 × 100) : 200,000 = 0.002 per cent (approx.). The expected content of phosphorus in the metal will be 0.023 + 0.002 = 0.025 per cent.

Practical recommendations on introducing ferro-alloys are given in Table 52.

Chapter Nineteen

GASES IN LIQUID STEEL AND VARIATIONS OF THEIR CONTENT DURING MELTING AND TEEMING

The sources of gases in the liquid metal of a converter or open-hearth bath are trimmings, steel scrap, and rust which is a mixture of variously hydrated oxides $x\mathrm{FeO} \cdot y\mathrm{Fe_2O_3} \cdot$ $\cdot z\mathrm{H_2O}$. The rust decomposes during heating and melting of scrap and the gases evolved (oxygen and hydrogen) dissolve partially in the liquid metal and slag.

Conversion iron (either solid or liquid) also introduces hydrogen (around 2.5-3.0 cm^3 per 100 g of metal) and nitrogen (between 0.004 and 0.008 per cent).

The various ferro-alloys that are added to the liquid metal on tapping or in the ladle for deoxidation and alloying and synthetic mixtures added to the bath in the diffusion deoxidation are also gas carriers (Table 53). It is therefore advis-

Table 53

Hydrogen, Oxygen, and Nitrogen in Ferro-Alloys (according to various sources)

Ferro-alloy	Hydrogen, $cm^3/100$ g	Oxygen, %	Nitrogen, %
Nickel obtained by the Mond process	85-100	0.017	0.003
Ditto, after long storage	12-17	0.023	0.003
Ferro-silicon	8-38	0.019	0.005-0.01
Silico-calcium . . .	38	—	0.03
Ferro-chrome	6-16	—	0.012-0.043
Ferro-manganese . . .	13-35	0.002	0.02-0.05
Silico-manganese . .	40-80	—	0.019-0.039
Ferro-titanium . . .	46	0.155	0.008
Ferro-niobium	20	0.169	—
Ferro-tungsten	12	0.208	—
Ferro-molybdenum	6-10	0.039	0.002
Aluminium	—	—	0.001

able to temper ferro-alloys before adding them into the liquid metal.

The metal and slag also absorb gases from the fuel, air, and combustion products, which contain much of nitrogen, carbon oxides and water vapour. At the high temperature in the reaction chamber, dissociation of triatomic gases occurs, which is an additional source of hydrogen and oxygen. As the molten bath becomes fully covered with slag, any further penetration of gases into the metal depends on the protective properties of the slag. As has been found, gases can dissolve in slag. According to some experimental data, nitrogen cannot penetrate into the bath through an acid slag.

According to various investigations, the following amounts of gas have been found in the slags of various steelmaking processes, in percentages:

Nitrogen in the final slag:	
of a basic open-hearth melt	0.002-0.008
of an acid open-hearth melt	0.0015-0.003
of a basic electric-arc melt:	
carbide slags	up to 0.2
white slags	0.018-0.065
Hydrogen in the final slag:	
of a basic open-hearth melt	0.0023-0.0046
of an acid active open-hearth process	0.0016-0.0025
of a silicon-reducing open-hearth process . . .	0.0018-0.0016
Hydrogen in the slag of a basic electric-arc melt:	
at the end of the oxidation period	0.0014-0.0025
at the end of the reduction period under white slags	0.0045
ditto, under carbide slags	0.0052

The content of hydrogen and nitrogen in the metal reduces during vigorous boiling of the bath owing to the diffusion of these gases into bubbles of carbon monoxide. The stronger the boiling, the greater is the rate of removal of gases from the metal. But this type of gas removal can only be achieved under conditions of vigorous 'pure' boiling, i.e., without ore, bauxite, or other materials being added. Otherwise the moisture contained in ore and bauxite would promote saturation of the metal with hydrogen. Some nitrogen and hydrogen may also penetrate into the bath from the furnace atmosphere and from the slag with the beads of metal that have been erupted from the bath during very strong boiling when the slag 'runs off' the metal.

The different way of hydrogen behaviour in the liquid bath during the heat can be related to the concentration of carbon. In melts for mild grades of steel (in which carbon ceases to be a factor controlling the oxidation of the bath), the amount of hydrogen can be less as its solubility is lower in oxidized metal.

Figure 136 shows the relationship between the content of hydrogen and carbon in the bath during the heat in various steelmaking units, taking into account the degree of superheating of the metal above the liquidus line.

The above discussion makes it possible to formulate the principal regularities governing the behaviour of hydrogen during melts in basic open-hearth furnaces. Addition of dry iron ore and a high level of iron oxides in the slag at the beginning of the refining period promote the removal of hydrogen from the steel. Addition of lime during pure boiling may have a different effect on the behaviour of hydrogen in the metal. With carbon concentrations below 0.2 per cent the content of hydrogen in the metal does not increase, and in certain cases falls off. With a higher carbon content the behaviour of the gases in the bath depends on the rate of oxidation of carbon and the properties of the slag. When dry iron ore is added to the slag, the inflow of oxygen to the metal increases, so that the upper layers of the metal become more oxidized and absorb less hydrogen. This is particularly observed at the end of heats for mild steel, when the amount of oxygen in the metal increases. With smaller contents of iron oxides in the slag (which is observed in melts for medium- and high-carbon steels), the reduction of manganese begins and at the same time the absorption of hydrogen by the metal increases since the inflow of oxygen from the slag to metal decreases.

Acid open-hearth slag is characterized by a high viscosity and good wettability by the metal, so that it does not run off from the latter during boiling. Its capacity to protect the metal against penetration of gases, especially of nitrogen, is very high, because of which acid open-hearth steels are less saturated with gases, particularly with hydrogen, and therefore less liable to flaking and woody fracture.

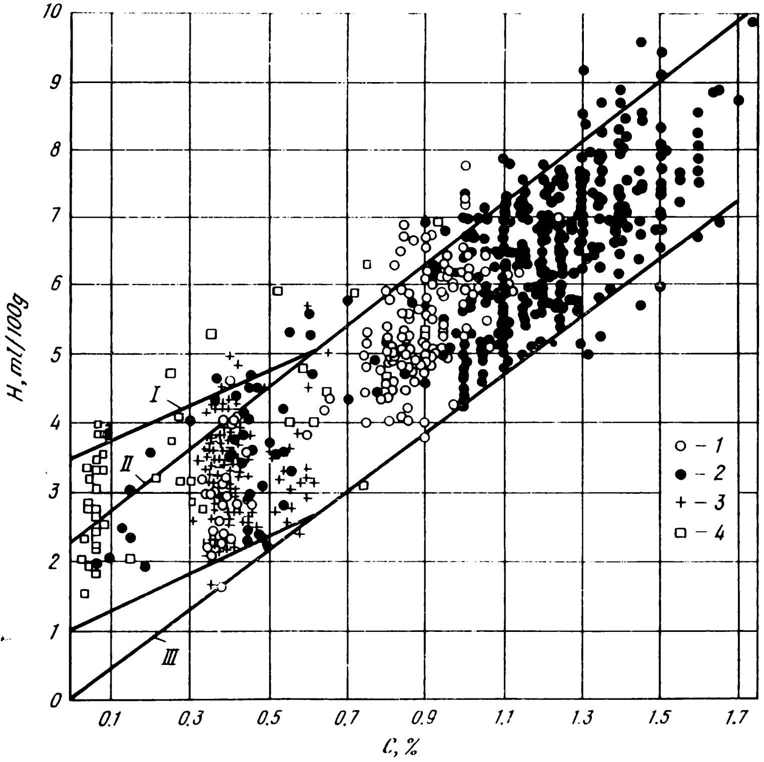

Fig. 136. Dependence of the hydrogen content during boiling of the bath on carbon content

1—basic open-hearth furnace; *2*—acid open-hearth furnace during melting; *3*—ditto, before deoxidation; *4*—basic electric furnace; *I*—slight superheat above the liquidus line; *II*—superheat by 100°C above the liquidus line; *III*—liquidus line

In basic furnaces run by the scrap-and-ore process the amount of hydrogen on meltdown is as high as 3.0-6.5 cm^3 per 100 g owing to the intensive gas evolution. In the pig-and-scrap process it is appreciably higher, reaching 3.0-8.0 cm^3 per 100 g, which may be explained by the longer contact of the charge with furnace gases, the smaller amount of oxidized carbon, and hence the smaller quantity of washing gases liberated from the bath.

The content of hydrogen in basic open-hearth slags may vary between 16 and 45 cm^3 per 100 g, i.e., is many times higher than in the metal.

As the oxidation of carbon reaches the critical rate during the period of active boiling, the concentration of hydrogen in the metal begins to fall off. With a higher temperature and longer period of pure boiling, the amount of gases, in particular, of hydrogen, in the metal becomes higher. In the period of preliminary deoxidation of the metal in the furnace, boiling is less intensive so that the gas content of the metal (including hydrogen) may increase.

The content and composition of gases in the metal vary substantially during tapping, which is usually accompanied by partial intermixing of the metal and slag at the end of tapping, so that the metal picks up some air. Pouring the metal into the ladle in an interrupted stream causes chilling of the metal, which reduces the solubility of gases but, on the other hand, oxidizes the metal owing to its contact with the atmospheric oxygen. The sharp fall of the partial pressure of water vapours above the metal in the ladle as compared with the furnace atmosphere also causes a change in the hydrogen content of the metal.

The amount and composition of the gases in the metal alter further during teeming because of chilling and oxidation of the stream. The method of teeming, whether direct or uphill, also affects the saturation of steel with gases. For instance, in direct pouring the stream of metal is in contact with the air for a long time; in uphill teeming this period is shorter, but air is entrained through the central pipe; in both cases the total amount of gases in the metal increases and their concentrations alter.

These processes, plus the introduction of gases with ferro-alloys (and of oxygen in the form of non-metallic inclusions), are responsible for the different gas contents of samples taken before and during tapping. The content of hydrogen in the metal on teeming is sometimes 1-2 cm^3 lower (per 100 g metal) than in samples before tapping, especially if the teeming ladle has been well slagged, while the contents of oxygen and nitrogen are usually higher.

The amount of hydrogen in ladle samples of medium-carbon or low-alloyed killed steel is usually 3-8 cm^3 per

100 g metal, and of rimming steel, 3 cm^3 per 100 g. The concentration of nitrogen is 0.003-0.008 per cent.

SOLUBILITY OF GASES IN STEEL

Gases (oxygen, hydrogen, nitrogen, etc.) are soluble in metal. They may be present in the solution as separate atoms or ions or combined chemically with certain impurities in the metal. The absorption of gases through the formation of chemical compounds is substantially higher than that through the formation of interstitial solutions.

The processes of the uptake and dissolution of gases in the metal can be represented as follows. Particles of the gaseous phase collide with the surface of the liquid so that their molecules are adsorbed and dissociated into atoms. Atoms of the gas then dissolve in the bulk of metal. The concentrations of the gases dissolved in the metal are equalized owing to mass transfer, but true equilibrium is never attained.

The rate of dissolution of a gas in the metal is determined by its rates of dissociation and removal from the surface into deeper layers of the metal. Its rate of passage into the metal increases with an increase of the bath temperature, since the diffusion coefficient is then higher and viscosity lower.

The dependence of the solubility of hydrogen in metals on temperature is expressed by Borelius' formula:

$$S = Ce^{-\frac{E_S}{2KT}}$$

where S = solubility of gas in metal
C = constant
E_S = heat of formation of a solution or chemical compound of the gas with the impurities in the metal
K = Boltzmann's constant
T = absolute temperature

As can be seen from Fig. 137, the solubility of hydrogen in chromium, nickel, copper, aluminium, manganese, and cobalt increases with temperature, which shows that the processes of gas dissolution in these metals are endothermic.

Copper, silicon, cobalt, and chromium have approximately the same capability for dissolving hydrogen in a wide temperature range, though substantially lower than nickel, manganese or aluminium.

The solubility of hydrogen in such metals as titanium, zirconium, and vanadium falls off with an increase of temperature, i.e., the process is exothermic here.

As has been found from laboratory experiments, the solubility of hydrogen in liquid iron falls off in the presence of carbon, silicon, aluminium, chromium, and tungsten and increases in the presence of manganese, titanium, cerium, and niobium. In both cases the concentration of these elements affects hydrogen solubility. But since the steel after tapping from an open-hearth furnace or converter and after deoxidation and alloying usually contains not more than 1-2 per cent of alloying elements (and only rarely 3-4 per cent), the solubility of hydrogen and nitrogen in it is practically the same as in pure iron (Fig. 138).

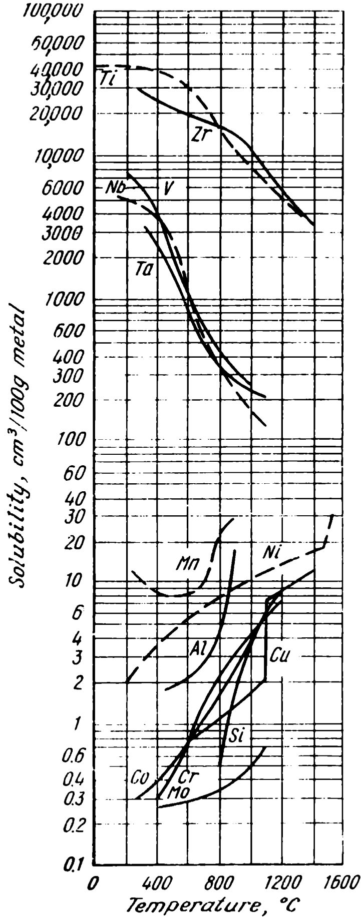

Fig. 137. Solubility of hydrogen in metals as a function of temperature

As has been found by Siverts, the solubility of a gas in metal at a given temperature is proportional to the square root of its partial pressure in the gaseous phase. This deviation from Henry's law (of direct proportionality) may be explained either by dissociation of the gas molecules into two atoms, which dissolve separately in the metal, or by the formation of a chemical compound in which each molecule contains only one atom of the dissolved gas.

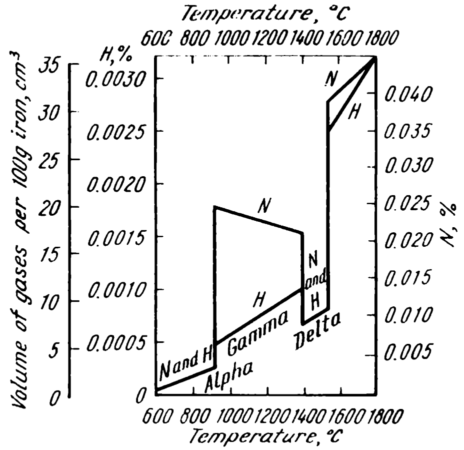

Fig. 138. Solubility of hydrogen and nitrogen in iron at atmospheric pressure as a function of temperature

The presumed reactions for nitrogen and hydrogen can be written as follows:

$$N_{2_{gas}} \rightleftarrows 2[N]_{sol};\quad K_N = \frac{[N]^2}{p_{N_2}}$$

$$H_{2_{gas}} \rightleftarrows 2[H]_{sol};\quad K_H = \frac{[H]^2}{p_{H_2}}$$

Hence the solubility of nitrogen in iron is

$$\%\,[N]_{Fe} = K_N \sqrt{p_{N_2}}$$

and that of hydrogen

$$\%\,[H]_{Fe} = K_H \sqrt{p_{H_2}}$$

where % [N], % [H] = nitrogen and hydrogen content of iron, per cent by mass

p_{N_2}, p_{H_2} = partial pressure of nitrogen and hydrogen in the gaseous phase, at

K_N, K_H = equilibrium constant of dissolution of nitrogen and hydrogen in iron

Thus, the concentration of a dissolved gas is proportional to the square root of its partial pressure.

Upon reacting with iron, nitrogen forms two compounds, Fe_4N and Fe_2N. The process may be described as follows:

$$2\{N\} + 8Fe \rightarrow 2Fe_4N$$

The solubility of a gas (hydrogen or nitrogen) depends on temperature (see Fig. 138), increasing sharply when the metal transforms from the solid to the liquid state and changing at transitions of α-Fe into γ-Fe and of γ-Fe into δ-Fe. The solubilities of hydrogen and nitrogen at 1600°C and a pressure of 1 at are respectively 0.0027 and 0.039 per cent. With further rise of temperature the solubility of hydrogen in molten iron increases faster than that of nitrogen.

The solubility of hydrogen in metal is usually given in the specialist literature in cubic centimetres per 100 grams of metal. Recalculation to percentages can be done by using the equality 0.0001 per cent = 1.12 cm^3 per 100 g.

The solubility of nitrogen in molten iron falls off with an increase of oxygen, phosphorus and carbon in the metal. Molybdenum, manganese, chromium and vanadium, on the contrary, favour its dissolution in molten iron.

Vacuum degassing outside the furnace and blowing of the metal in the ladle with inert gases (argon, helium, etc.) are now used with success. These methods make it possible to reduce the contents of oxygen and hydrogen in steel by 30-40 per cent and at the same time to lower the residual concentrations of non-metallic inclusions. For the same purpose, steel is cast at some works into heavy ingots in vacuum, i.e., with degassing of the stream of steel.

As has been found, apart from the formation of an interstitial solution, the dissolution of nitrogen in steel may be accompanied with the formation of nitrides, which is indicated by a high absolute concentration of this gas in the solution and high heats of formation of nitrides of some elements, for instance, chromium, aluminium and titanium nitrides, which are respectively equal to —28,300; —64,000; and —80,000 cal/mole.

With iron, nitrogen forms nitrides Fe_4N and F_2N. The most stable nitrides in liquid steel are those of titanium and zirconium. Nitrides of aluminium, vanadium and boron are formed at temperatures below the solidification point of the metal and are stable under these conditions. These elements can therefore reduce the concentration of dissolved nitrogen by converting it into nitrides.

The solubility of nitrogen in α-Fe is negligible at low temperatures, so that the gas dissolved in steel forms a supersaturated solution on cooling. Cold working and heating of the metal to 200-300°C cause the finely dispersed particles of nitrides to separate out of the solution at grain boundaries, in particular, of aluminium nitrides, if the steel has been deoxidized with aluminium. The result is that internal stresses develop in the metal, reducing its plastic properties, particularly its impact strength, i.e., causing its ageing.

The amount of nitrogen combined in nitrides increases with an increase of the residual content of nitride-forming elements in steel. Therefore, when making steels for deep stamping, it is best to control the degree of oxidation of the metal so as to avoid use of a large amount of nitrogen stabilizers, since nitrides segregate easily and contaminate the tops of ingots. When analysing a steel for nitrogen by the 'moist' method, it must be taken into account that zirconium, titanium, boron and vanadium nitrides are insoluble in hydrochloric and sulphuric acid which are usually employed for dissolution of carbon steels. Thus, if stable nitrides are present in the steel, the results of the analysis will be on the low side.

Oxygen dissolves well in liquid steel. Its solubility is possibly restricted by the formation of a liquid phase of ferrous oxide. The calculated pressure of oxygen at which this phase appears is 0.8×10^{-8} at at 1600°C. Such a low pressure cannot be measured by ordinary techniques. For that reason, the solubility of the oxygen present in metal is considered in terms of ferrous oxide.

The state in which oxygen is present in liquid iron upon dissolution is still not certain. The existence of FeO molecules in liquid iron seems improbable. It is more likely that oxygen dissolves in iron in the form of O^{2-} anions, rather than as oxides Fe_2O, Fe_3O, or Fe_xO.

The dependence of the solubility of oxygen (in the form of ferrous oxide) in liquid iron on temperature through the effect of pure oxides being out of contact with the crucible walls during the experiment is shown in Fig. 139.

The solubility of oxygen in solid iron at 900°C is 0.03 per cent. With a further fall in temperature the oxygen separates from the solution and forms oxide inclusions. As can be seen from Fig. 139, its solubility changes sharply with the transition from γ-Fe to α-Fe, which is accompanied by its separation from the solution in the form of iron oxides that cause ageing of steel.

Pure iron has a melting point of 1539°C; it becomes less fusible as the amount of oxygen dissolved in it increases, its melting point dropping to 1524°C with 0.16 per cent oxygen.

The amount of oxygen (dissolved oxygen plus oxides) in final solid steel is negligible and depends on the composition of the steel and the method of melting. For instance, an acid open-hearth steel with 0.5-0.6 per cent C contains 0.001-0.008 per cent O_2; a basic killed steel with the same carbon content has 0.002-0.003 per cent oxygen, and a basic rimming steel with 0.08-0.10 per cent C contains 0.018-0.020 per cent O_2.

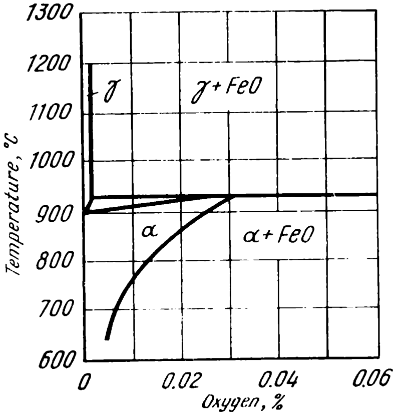

Fig. 139. Solubility of oxygen in γ-Fe and α-Fe at various temperatures

EVOLUTION OF GASES FROM SOLIDIFYING STEEL. FORMATION OF BLOWHOLES

The phenomenon of gas evolution from cooling steel has long been known, and steelmakers have sought ways to reduce the formation of blowholes in ingots.

Experiments in recovering gases evolved from the metal have shown that they consist of 65-90 per cent H_2, 10-30 per cent N_2, and 0.5-2.59 per cent CO. Later experiments have established that a large amount of gases liberates also from killed steel and pig iron, as well as from rimming steel.

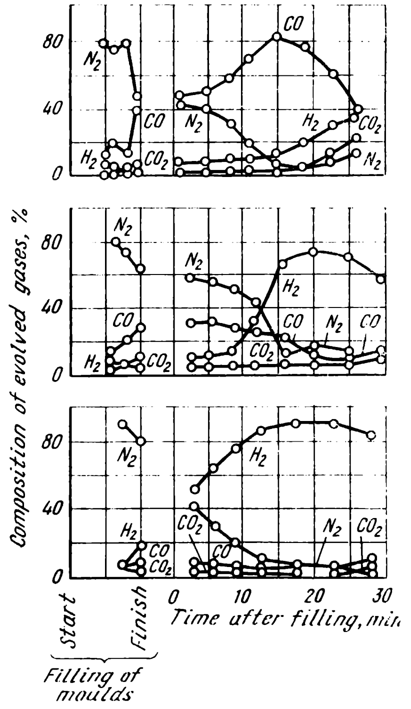

Fig. 140. Composition of gases liberated from steel during solidification

a—rimming steel (0.08% C); *b*—semi-killed steel (0.10% C); *c*—killed steel (0.10% C, 0.15% Si, 0.05% Al)

The gases evolving from liquid or solidifying metal also contain methane and carbon dioxide in addition to carbon monoxide, hydrogen, and nitrogen. These two gases are the products of secondary reactions of oxygen with CO and hydrogen by the reactions $CO + O = CO_2$ and $2CO + 2H_2 = CH_4 + CO_2$ with the formation of CO_2 and CH_4.

When silicon is added to boiling steel, the composition of gases varies sharply since there is very little oxygen left to react with the carbon. This explains why gases are liberated from any kind of steel: killed, semi-killed or rimming (Fig. 140). But less gas having a negligible content of carbon monoxide is liberated from killed steel, owing to a low concentration of oxygen dissolved in it.

With more intricate experimental techniques employed, it has been possible to determine the composition of the gases in blowholes in individual crystalline zones of rimming-steel ingots. The gases taken from the zone of honeycomb blowholes in the lower part of an ingot contain 80 per cent H_2, 4 per cent CO, 11 per cent N_2, and 5 per cent CH_4; secondary blowholes are mainly filled with carbon monoxide; central blowholes contain much nitrogen.

The results of the experiments with 800-kg ingots of rimming steel are given in Table 54.

Table 54

Composition and Quantity of Gases Liberated During Solidification of an 800-kg Rimming-Steel Ingot

Time from end of mould filling, min	Rate of evolution, litres/min	Total quantity of gas, litres	Content, percentages			
			CO_2	CO	H_2	N_2
0.5	14.4	—	2.4	85.2	12.2	0.2
1	12.0	13.3	2.0	81.9	15.9	0.2
2	11.1	24.4		—	—	—
3	12.0	36.4	2.1	82.2	15.5	0.2
4	12.6	49.0	—	—	—	—
5	18.0	67.0	2.2	81.6	16.0	0.2
6	13.5	80.5	—	—	—	—
7	13.0	93.5	—	—	—	—
8	7.6	101.1	—	—	—	—
9	10.4	111.5	—	—	—	—
10	6.9	118.4	2.8	86.2	10.8	0.2
11	12.5	130.9	—	—	—	—
12	8.0	138.9	—	—	—	—
13	5.4	144.3	—		—	—
14	3.3	147.6	3.4	84.6	10.6	1.4
15	3.1	150.7	—	—	—	—
16	3.9	154.6	—	—	—	—
17	2.2	156.8	—	—	—	—
18	2.0	158.8	—	—	—	—
19	1.8	160.6	5.1	83.6	9.6	1.7
20	1.2	161.8	—	—	—	—
24	11.0 *	172.8	7.9	78.5	12.1	1.5

---

* Suction apparatus switched on.

The composition of the gas evolved during solidification from the peripheral zones was determined in an ingot cast on a neighbouring bottom plate. By using rheometers calibrated to a flow rate of 10 and 5 l/min, it was discovered that the rate of liberation varied intermittently (Fig. 141). It should also be noted that the switching on of a suction apparatus caused a sudden increase in the rate of gas evolution. It was also found that the amount of gas liberated at positive pressures was 0.25 m^3/t, or approximately one-tenth of that in experiments with gas extraction.

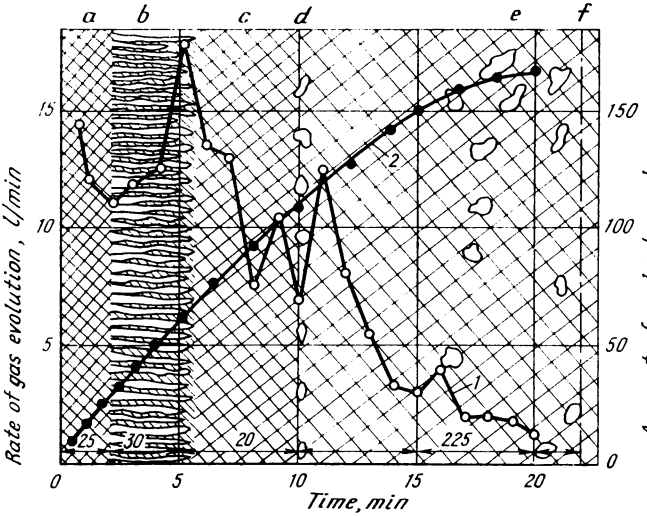

Fig. 141. Gas formation in an 800-kg ingot of rimming steel during solidification

1—rate of gas evolution, l/min; *2*—amount of evolved gases, l; *a*—dense crust; *b*—zone of honeycomb blowholes; *c*—layer free from blowholes; *d*—secondary blowholes; *e*—central blowholes; *f*—axis of ingot

Investigation of the crystalline structure and heterogeneity of ingots cut along their axis established a connection between the formation of ingot structure in the initial period of solidification and the process of gas evolution (see Fig. 141). By using the data on the heterogeneity of that ingot, it was established that the solidification occurs initially at a high rate, with the result that segregation of impurities and oxygen is insignificant. The absence of segregates capable of forming gaseous reaction products in that time interval is reflected in Fig. 141 as a reduction in the rate of gas liberation. Only when segregates have accumulated in the layer of liquid metal adjoining the solid phase, which is connected with the drop in crystallization rate after the formation of the initial blowhole free crust, does a secondary rise in the rate of gas evolution begin. The directional growth of dendrites, however, outstrips the evolution of gases and hampers the escape of the bubbles formed which are trapped in the capillaries between crystallites and later serve as the basis for the development of honeycomb blowholes.

Thus, it has been found that honeycomb blowholes form in rimming-steel ingots during strong evolution of gases, in which the main constituent is carbon monoxide (80-85 per cent). During solidification of the intermediate zone (between honeycomb and secondary blowholes), the rate of liberation of gases falls off owing to the change in solidification conditions, i.e., owing to the formation of blowholes under the skin after the ingot has detached from the walls of the mould. For that reason gases can escape from that zone of the ingot without forming blowholes.

Intense evolution of gases, accompanied with an upward flow of the metal, promotes the transfer of segregates to the top of the ingot, so that the composition of the components in the layer of metal adjoining the solid phase (except in the head of the ingot) becomes more or less equalized and no noticeable heterogeneity is detected by chemical analysis in the solidified zone between honeycomb and secondary blowholes in lower sections of the ingot.

The formation of secondary blowholes is due to the fact that the initial strong evolution of gases is attenuated and its rate is gradually decreased.

The nitrogen dissolved in the liquid metal cannot form bubbles since its concentration is much lower than its solubility in solid steel.

It is probable that a process of separate formation of hydrogen bubbles may develop at the boundary of the front of solidification when the solubility limit of hydrogen in solid steel has been substantially exceeded. This occurs at least in the two-phase zone owing to the segregation of impurities, including hydrogen. Nitrogen and hydrogen diffuse into the formed bubbles of carbon monoxide, in which their partial pressures are extremely low.

As steel solidifies in a mould, bubbles of carbon monoxide form at the contact front of the liquid metal with solid crystallites, since pores are formed in the crystallites owing to shrinkage. These pores serve as centres for the formation of gas bubbles.

Not all pores, of course, can be active in the formation of gas nuclei. Their critical size depends on the carbon content of the metal. Calculations for an open-hearth melt with the bath one metre deep, a temperature of 1600°C and a wetting angle of 90 degrees have shown that pores can become active when their size is of an order of 10^{-2} cm. With substantially larger wetting angles, the work of bubble formation is minimal and thereby the intensity of their formation increases.

A bubble formed in an active pore grows until the Archimedian lifting force, which increases as the bubble grows, exceeds the forces of cohesion with the particles of the metal at the bubble-metal boundary along the perimeter of the neck formed, after which the bubble breaks away from the pore and floats up. A nucleus remains at the point of rupture which grows into a new bubble. The result is that each active pore continues to form gas bubbles until its size corresponds to the current concentration of carbon (oxygen).

Solid inclusions in the metal, if they have a rough surface or shrinkage cracks of suitable critical size, can also become centres of bubble formation. Consequently, there always are conditions during the solidification of a rimming steel having a sufficiently high concentration of dissolved oxygen for the formation of gas nuclei and bubbles.

Thus, solidification of rimming steel provides favourable conditions for the formation of nuclei of gas bubbles. But this is still not sufficient for the formation of bubbles proper. Conditions must be provided for the growth of nuclei. Nuclei can only grow into bubbles when the concentrations of carbon, oxygen, hydrogen and nitrogen in the metal exceed the values corresponding to their equilibrium with CO, H_2 and N_2 in the nucleus, The conditions for the formation of bubbles are as follows:

$$[\%\,\mathrm{C}]\cdot[\%\,\mathrm{O}]\,K'_{\mathrm{C}} > p_{\mathrm{CO}}$$

$$\frac{[\%\,\mathrm{H}]^2}{K_{\mathrm{H}}^2} > p_{\mathrm{H}_2};\ \frac{[\%\,\mathrm{N}]^2}{K_{\mathrm{N}}^2} > p_{\mathrm{N}_2}$$

where p_{CO}, p_{H_2}, and p_{N_2} = partial pressures of CO, H_2, and N_2 in a gas nucleus
K'_{C}, K_{H}, and K_{N} = equilibrium constants of the corresponding reactions

Since the sum of p_{CO}, p_{H_2} and p_{N_2} is equal to the total pressure in the nucleus, which is made up of the atmospheric, ferrostatic and capillary pressures, the conditions in which gas bubbles can form in the metal may be expressed by an inequality:

$$[\%\,\mathrm{C}]\cdot[\%\,\mathrm{O}]\,K'_{\mathrm{C}} + \frac{[\%\,\mathrm{H}]^2}{K_{\mathrm{H}}^2} + \frac{[\%\,\mathrm{N}]^2}{K_{\mathrm{N}}^2} > 1 + h\rho + \frac{2\sigma}{r}$$

where h = height of the column of liquid metal above the nucleus
ρ = density of liquid metal
σ = surface tension of liquid steel
r = bubble radius
$2\sigma/r$ = capillary pressure

As will be seen from this inequality, the higher the concentrations of carbon, oxygen, hydrogen, and nitrogen in the metal, the lower will be the depth at which bubbles can form and the smaller will be the size of nuclei capable of forming bubbles.

Steel will be killed and the formation of bubbles completely excluded when

$$[\%\,\mathrm{C}]\cdot[\%\,\mathrm{O}]\,K'_{\mathrm{C}} + \frac{[\%\,\mathrm{H}]^2}{K_{\mathrm{H}}^2} + \frac{[\%\,\mathrm{N}]^2}{K_{\mathrm{N}}^2} < 1$$

i.e., when the largest nuclei cannot grow in the upper portion of an ingot (in that case capillary pressure is negligible and ferrostatic pressure is close to zero). When the sum of partial pressures becomes unity, the number of bubbles being formed at greater depth will increase and they will be formed from smaller nuclei, i.e., the intensity of gas evolution will rise. When the value indicated is exceeded, the conditions will exist for the formation of an ingot of semi-killed steel, and with a further increase, conditions for the formation of a rimming-steel ingot (Fig. 142).

But, as indicated above, the amounts of hydrogen and nitrogen usually found in steel lie within very narrow and insignificant limits, and the predominance (around 90 per cent) of the sum on the left-hand part of the inequality given above comes to [% C]·[% O]·K'_C. With a known carbon content, the magnitude of this product is therefore mainly determined by the concentration of oxygen in the steel.

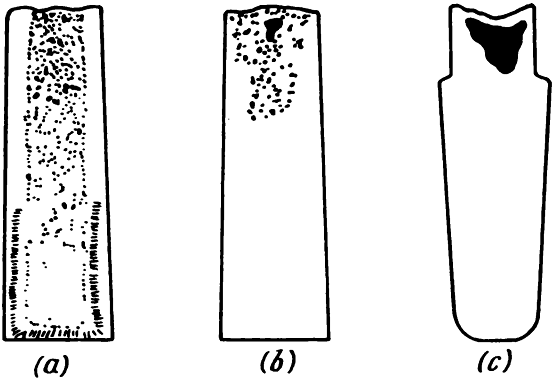

Fig. 142. Structure of ingots of (a) rimming, (b) semi-killed and (c) killed steel

Thus, the nature and intensity of gas evolution, for the same rate of solidification of steel in a mould, are determined by the concentration of dissolved oxygen, i.e., the type of the ingot obtained can be controlled by varying the amount of oxygen dissolved in the metal.

Further degassing of the metal is much easier, since the bubbles permeating the whole volume of the metal form large areas of interphase boundaries of high activity and thus serve as centres of gas formation. The rate of floating up depends on the radius and shape of bubbles. As with non-metallic inclusions, bubbles can coalesce and grow through collision. Cooling of the metal during solidification promotes intensification of gas evolution, since the solubility of gases falls. On the other hand, the viscosity of the liquid metal increases with a fall in temperature, thus impeding the rise of bubbles.

The height of an ingot is of no small importance for gas evolution. The taller the ingot, the more unfavourable are the conditions for boiling of the metal in the mould. Other conditions (temperature, viscosity, composition, and oxidation of the metal) being equal, the taller the ingot of rimming steel, the more gas is retained in it and the higher is the zone of honeycomb blowholes.

During the solidification of killed steel in which the concentration of dissolved oxygen after deoxidation is only negligible, the effective collision of carbon and oxygen with the formation of CO bubbles is impossible. Nitrogen and hydrogen diffuse in this steel to the surface of the metal in the mould or to the surface of the ingot, where they are desorbed after molecular transformations. But since the rates of diffusion in quiet metal are low, the amount of gases evolved per unit time from undisturbed killed steel is also low.

To determine the effect of teeming speed on the intensity of gas evolution, experiments were carried out with casting electric killed steel uphill on two-mould and six-mould bottom plates. The results obtained suggested the following conclusions:

(1) the rate of gas evolution reaches a maximum just as the mould has been filled with metal and then falls abruptly;

(2) the main constituents of the gas evolved are hydrogen and carbon monoxide;

(3) the volume of gas evolved is directly proportional to the time of filling the mould;

(4) the volume of gas liberated remains practically constant after the teeming is completed.

EFFECT OF GASES ON THE PROPERTIES OF STEEL

After steel has solidified, the gases in it may be in solid solution, or as bubbles, hydrides of certain elements, nitrides, or oxides. A steel properly degassed and killed with strong deoxidants contains no blowholes. But cases are sometimes observed when ingots grow (for instance, those of transformer steel, which, as is known, contains much silicon). Sometimes strong evolution of gases is observed during solidification of steels containing more than one per cent aluminium. These abnormalities are connected with the use of moist ferro-silicon for deoxidation, which increases the amount of hydrogen in the steel in the final production stages.

The subcutaneous blowholes found in ingots have no connection with the gases remaining in the steel, but are the result of the gas formation during the rise of the metal in the mould. The accumulation of gases in the upper central part of an ingot leads to the development of porosity and discontinuity of the metal. The development of segregation in killed-steel ingots in the form of 'whiskers' or ghost is also related to the effect of gases, in particular, of hydrogen. Gases in steel have a significant effect on the quality of ingots and later on the properties of the rolled product.

Oxygen. The amount of oxygen in steel at the moment of solidification determines what kind of steel will be produced: killed, semi-killed, or rimming.

The total amount of oxygen by the end of the heat after deoxidation is made up of the oxygen dissolved in the steel and of that found in the oxide inclusions which have not had time to separate out and are present in the steel in suspension. These oxides have been formed in the metal through oxidation reactions.

Since the amount of oxygen that can be dissolved in solid steel is much lower than in liquid steel (see Fig. 139), it separates out of the solution during solidification and promptly combines with the silicon and aluminium dissolved in the steel, thus forming undesirable oxide inclusions. As this happens in the last stage of the transition from the liquid to the solid state, it is impossible to expect these oxides to float up. Therefore, the steel obtained will be purer and its quality better if the total amount of oxygen in it (both dissolved and in suspension as oxides) at the moment of solidification is insignificant.

The effect of oxygen inclusions on the properties of steel will vary according to their composition and location. The most harmful are oxides distributed as chains, threads, or films along grain boundaries. These forms are most often observed in the formation of silica, corundum, and alumosilicate inclusions. Less harmful are spheroidal silicate inclusions which are formed just after addition of deoxidants.

A high oxygen content, as has been established, renders a steel liable to ageing, impairs its electrical resistivity, and lowers its magnetic properties owing to higher power losses. The effect of oxygen on ageing may be seen from the following example: the metal taken from the surface layer of a rimming-steel ingot with an oxygen content of 0.02 per cent proved less apt to age than the metal from the core of the same ingot where the oxygen content was 0.06 per cent. The tendency of steel to ageing was estimated by measuring the plastic properties of samples, and especially their impact strength, before and after artificial ageing, for which purpose samples were subjected to 10-per cent elongation with subsequent tempering for an hour at 250°C.

An increased content of oxygen in a tungsten magnet steel lowers the power of magnets. It is also known that a high percentage of oxygen in steel gives it red shortness even at a normal sulphur content. This phenomenon is linked with the fact that oxygen separates out of the supersaturated solution during solidification and that grains of metal are surrounded by an oxy-sulphide phase which weakens the bonds between them.

Hydrogen. The adverse effect of hydrogen on the quality of ingots has long been known. Evolution of hydrogen during solidification causes the development of riser in ingots, the formation of pores in both ingots and billets, and the development of ghost in ingots. Hydrogen segregates and accelerates the segregation of other impurities. Increased concentrations of hydrogen are usually found in the middle and top of ingots. With the capacity of hydrogen to segregate, there is always the danger of appearance of some of ingot defects.

As will be seen from Fig. 138, liquid steel can become supersaturated with hydrogen during its solidification and further cooling because of the different solubilities of hydrogen in the various modifications of iron. A large amount of hydrogen is liberated from the solution within the ingot (or casting) near finest fissures, in shrinkage discontinuities and in pores at the boundaries between non-metallic inclusions and the metal.

The molecular transformation $2\,[H] \rightarrow H_2$ developing there causes an accumulation of hydrogen molecules so that regions are formed in the solidified steel where this hydrogen is subjected to a considerable pressure, which encourages the rise of internal stresses in the metal. When these internal stresses are combined with others, for instance, thermal stresses or stresses due to phase transformations, or when the strains in the metal exceed the ultimate strength at a given state of the steel, internal fractures can occur and very fine fissures or flakes can form.

Chrome-nickel and chrome-nickel-molybdenum steels usually solidify with the development of columnar crystallites. This feature of their crystalline structure provides conditions for the accumulation of molecular hydrogen at the boundaries of developed crystallites, owing to which high stresses develop just there, weakening the bonds between crystallites and reducing the strength of the metal in lateral directions. The break usually has a dendritic (lamellar) structure known as lappiness. Low- and medium-carbon steels are less liable to this defect than steels alloyed with chromium, nickel or molybdenum. Lappiness impairs the plastic properties of steel.

In order to eliminate the harmful effect of hydrogen, steel is subjected to heat treatment, which provides conditions for its diffusion to the surface of the ingot (or casting) and further removal, whereby eliminating the possibility of accumulation of molecular hydrogen within the ingot. Development of the defects mentioned above can also be prevented by slow cooling of ingots in special arrangements or under hot sand.

Vacuum degassing of liquid steel, which reduces the concentration of hydrogen to 1.5-2.0 cm^3 per 100 g metal, completely prevents the formation of flakes, hairline cracks, and lappiness. This method has also confirmed that it is hydrogen that is the main cause of the formation of these defects in forgings, especially of alloyed steel. Another method widely employed for the same purpose is to blow the molten metal with inert gases (helium or argon) in the furnace or more often in the ladle through porous refractory cones in its bottom.

Nitrogen. As has been found, a high concentration of nitrogen increases the strength properties of steel and at the same time reduces its plastic properties. Nitrogen increases the brittleness and hardness of steel and tends to reduce its magnetic permeability. It has also been found that steels that have been deoxidized and alloyed with nitride-forming elements, e.g. titanium or zirconium, have a higher content of nitrides.

In combination with carbon, nitrogen makes steel inclined to ageing. The greatest loss of impact strength after artificial ageing is observed in rimming steels; a steel killed with silicon displays only a slight tendency to age, but the same steel deoxidized additionally by aluminium, is practically non-ageing. It is also known that carbon steel with a nitrogen content of 0.003 per cent and residual aluminium content of 0.02 per cent is non-ageing; for the same steel, with 0.007 per cent nitrogen, to retain its non-ageing properties it must have a residual aluminium content of 0.035 per cent. Non-ageing can also be ensured in steels by small amounts of residual vanadium (0.02-0.04 per cent).

Basic Bessemer rimming steel with as high as 0.03 per cent nitrogen has the highest tendency to age. Killed steel with 0.20 per cent carbon, deoxidized by silicon and aluminium, is almost non-ageing. Rimming steel with 0.05 per cent carbon and no aluminium, i.e., saturated with gases including nitrogen, ages rapidly. Semi-killed steel is less liable to age than rimming steel, and when additionally deoxidized by aluminium, is only slightly prone to ageing. There are also indications that it is possible to use small additions of boron (0.005 to 0.006 per cent) to bind nitrogen in rimming and semi-killed steels in order to improve their non-ageing properties.

As follows from Fig. 138, the solubility of nitrogen in steel falls abruptly with lowering of temperature. Nitrogen then inevitably liberates from the liquid metal as the latter cools and solidifies. The free nitrogen segregates, like carbon, phosphorus or sulphur, during the solidification of the metal and accumulates in the middle and top of the ingot. Nitrogen separates out of the supersaturated regions of the metal as nitrides stable both at high and low temperatures. The finely dispersed separated solid phase of nitrides and carbides gives rise to crystal lattice defects which encourage ageing.

Nitrogen is sometimes deliberately introduced into steel. For instance, addition of nitride-forming elements to a steel containing nitrogen encourages the formation of a fine-grained structure since the nitrides formed act as nucleation centres. Techniques are also known for preventing transcrystallization in high-chromium steels by adding nitrated ferro-chrome or ferro-manganese to yield 0.3 per cent nitrogen in the final steel, which leads to the formation of chromium nitrides, prevention of transcrystalline structure, and the formation of fine grains.

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